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14. ABSTRACT

This report results from a contract tasking Universidad Autonoma de Madrid as follows: Slater orbitals provide a well-known basis for efficient descriptions of the atomic and molecular eigenstates required in studies of chemical structures and related properties. A series of studies [J. Comp. Chem. 25, 1987 (2004)] describes a computational code suite (SMILES) for calculations of molecular integrals which overcomes many of the difficulties that have previously precluded wide-spread adoption of Slater-based methodology for these purposes. This work attempted to extend the capabilities of the SMILES suite to principal quantum numbers at least N=10, and possibly higher, for all orbital angular momentum values in the range L= 0 to 5, while obtaining accuracy of at least ten significant figures for all integrals in the SMILES groups 1 through 6 [J. Comp. Chem. 25, 1987 (2004)], with somewhat lower accuracy acceptable for integrals in Groups 7 through 9. The algorithms for computing molecular integrals with Slater functions implemented in the SMILES package for molecular calculations have been thoroughly analyzed regarding the accuracy and computational cost for high quantum numbers and in a wide range of screening factors. Alternative algorithms have been developed for those cases in which the old algorithms are not suitable for the range of exponents and quantum numbers considered. The new algorithms have been coded and their performance has been thoroughly tested.

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Molecular Slater Integrals for Electronic Energy Calculations

(Final report on the project funded by EOARD, Grant 093069)

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Abstract

The algorithms for computing molecular integrals with Slater functions implemented in the SMILES package for molecular calculations have been thoroughly analyzed regarding the accuracy and computational cost for high quantum numbers and in a wide range of screening factors. Alternative algorithms have been developed for those cases in which the old o algorithms are not suitable for the range of exponents and quantum numbers considered. The new algorithms have been coded and their performance has been thoroughly tested.

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1 Introduction

Slater orbitals provide a well-known basis for efficient descriptions of the atomic and molecular eigenstates required in studies of chemical structures and related properties, and are potentially applicable to a wide range of AFRL and other DoD branch interests. A recent series of studies[1, 2] describes a computational code suite (SMILES) developed in our group for calculations of molecular integrals which overcomes many of the difficulties that have previously precluded wide-spread adoption of Slater-based methodology for these purposes.

The SMILES methodology in present form is largely applicable to the orbital principal quantum numbers required for accurate descriptions of the valence shells of atoms and molecules, and is therefore highly suitable largely for studies of ground-state molecular structure and low-lying valence excited electronic states. Highly excited molecular electronic states, however, are of considerable interest in a great many connections, including optical spectroscopic diagnostics for identification and characterization of newly synthesized chemical compounds for propulsion and energetics[3], studies of photochemical potential energy surfaces for atmospheric and related reactions[4], descriptions of molecular Rydberg and continuum states required in photon and electron-impact excitation processes [5], and in calculations which require spectral closure over electronic states, such as the long-range interactions required in atomic and molecular cluster studies[6], to mention some representative examples.

Extension of SMILES methodology to higher principal quantum numbers would open the way to development of a great many new computational applications suites which can provide concomitant support to on-going DoD materials, chemical physics, and aeronautical and propulsion sciences research programs. This extension requires a thorough revision on the performance of the algorithms currently available and the design of new alternatives for those cases in which the current algoritms are not well suited for large quantum numbers.

The currently available SMILES methodology is satisfactory for atomic orbital involving usual values of screening factors and angular momentum quantum numbers, L, ranging from 0 to 5, with allowable principal quantum numbers, N, from 1 to $7 - L$.

The methodology has been tested in a high amount of molecular calculations dealing with the ground and low-lying excited states in molecules for standard equilibrium geometries. However, the performance of these algorithms in less usual situations, as those requiring very high or very small screening constants and higher quantum numbers, has not been examined to date.

The current work starts with the thorough analysis of the performance of the algorithms currently implemented in SMILES in a wide range of values of screening constants and for moderately high values of quantum numbers. In those cases in which the algorithms do not provide sufficient accuracy, other alternatives are formulated and coded, and their performance is tested in order to assess their capability to overcome the existing ones.

The work has been developed in steps corresponding to the cathegories of integrals appearing

in molecular calculations. In each step, a robust code, usually lengthy for practical pruposes but good enough for a reference, has been developed to provide a reliable reference in testing.
Once the code for the reference has been implemented, integrals corresponding to appropriate quantum numbers have been computed for a wide set of screening parameters. The currently available algorithms and the reference program have been used for this purpose, and a thorough comparison on accuracy has been carried out. In those cases in which the current algorithms have revealed unsatisfactory, alternative procedures have been formulated, coded and tested.
In all cases, even for the algorithms already available in SMILES, new codes in FORTRAN 90 have been developed in order to allow their extension to quadruple precision and multiprecision (mainly for the reference). In some cases, this has implied drastic modifications in the codes with respect to the original ones, with new algorithms for the computation of auxiliary functions and a significant storage reorganization.
In the following sections, after a summary of the basic definitions and concepts, the fundamentals of the techniques applied for solving the integrals are described and the algorithms analyzed for each type of integrals are reported. To make the text more readable, results and conclusions are presented and commented within each type of integrals.
The report ends with a list of the programs developed. The files containing the source codes can be found as supplementary material accompanying this report.

2 Basic concepts

LCAO *ab initio* calculations of the electron structure of molecules require four types of integrals: overlap, S_{rs}, kinetic energy, T_{rs}, nuclear attraction, V^I_{rs}, and electron repulsion, v_{rstu}.
For a given basis set: $\{\chi_r\}_{r=1}^m$, they are defined respectively by:

$$S_{rs} \equiv \int d\mathbf{r}\ \chi_r(\mathbf{r})\ \chi_s(\mathbf{r}) \equiv \langle\, \chi_r \,|\, \chi_s \,\rangle \tag{1}$$

$$T_{rs} \equiv -\frac{1}{2}\ \int d\mathbf{r}\ \chi_r(\mathbf{r})\ \nabla^2\chi_s(\mathbf{r}) \equiv \langle\, \chi_r \,|\, \hat{T} \,|\, \chi_s \,\rangle \tag{2}$$

$$V^I_{rs} \equiv -Q_I\ \int d\mathbf{r}\ \frac{\chi_r(\mathbf{r})\ \chi_s(\mathbf{r})}{|\mathbf{r}-\mathbf{R}_I|} \equiv \langle\, \chi_r \,|\, \frac{-Q_I}{r_I} \,|\, \chi_s \,\rangle \tag{3}$$

where Q_I is the charge of nucleus I, and

$$v_{rstu} \equiv \int d\mathbf{r}\ \chi_r(\mathbf{r})\ \chi_s(\mathbf{r})\ \int d\mathbf{r}'\ \frac{\chi_t(\mathbf{r}')\ \chi_u(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \equiv [\, \chi_r\, \chi_s \,|\, \chi_t\, \chi_u \,] \tag{4}$$

As the definitions render evident, molecular integrals can be classified into two main cathegories attending the dimension of the integrals: one-electron (3D) and two-electron (6D). It is also well known that the difficulties found in the evaluation of integrals with STO strongly depend on the

number of centers of the functions. According to this number, they are further divided in one, two, three and four-center integrals.

This report deals with the calculation of molecular integrals involving exponential functions known as Slater type orbitals (STO). An unnormalized STO centered at a point $\mathbf{R}_A$ is a product of a regular (real) harmonic times a radial factor:

$$\chi^n_{LM}(\zeta, \mathbf{r}_A) = z^M_L(\mathbf{r}_A)\; r_A^{n-1}\; e^{-\zeta\, r_A} \tag{5}$$

where $\mathbf{r}_A = \mathbf{r} - \mathbf{R}_A$, n is a nonnegative integer and

$$\begin{aligned} z^M_L(\mathbf{r}) &= r^L\; z^M_L(\theta,\phi) = (-1)^M\; r^L\; P^M_L(\cos\theta)\; \cos M\phi \qquad 0 \le M \le L \\ z^{-M}_L(\mathbf{r}) &= r^L\; z^{-M}_L(\theta,\phi) = (-1)^M\; r^L\; P^M_L(\cos\theta)\; \sin M\phi \qquad 1 \le M \le L \end{aligned} \tag{6}$$

where $P^M_L(\cos\theta)$ denotes a Legendre function (see [7] Eq 8.751.1). Notice that index n *is not* the usual N quantum number, but it is related to it by: $n = N - L$. Index n is useful to simplify the notation in many equations.

STO can be normalized by multiplying by the norm factor:

$$N^n_{LM} = \sqrt{\frac{2L+1}{2\pi\,(1+\delta_{M,0})}\;\frac{(L-|M|)!}{(L+|M|)!}\;\frac{(2\zeta)^{2n+2L+1}}{(2n+2L)!}} \tag{7}$$

Eqs(1) to (4) show that molecular integrals depend on products of two functions rather than on functions themselves. These products:

$$D^{nn'}_{LML'M'} \equiv \chi^n_{LM}(\zeta, \mathbf{r}_A)\; \chi^{n'}_{L'M'}(\zeta, \mathbf{r}_B) \tag{8}$$

will be called *charge distributions* (or simply *distributions*) in the sequel, a name coming from the role played by these quantities in the integrals.

Details on properties of STO and their charge distributions are given in reference [2].

3 Ellipsoidal coordinates

As it is well known, ellipsoidal coordinates are often a good choice to deal with systems having cylindrical symmetry. Since this is the case of all the two-center integrals, several algorithms developed for these integrals are formulated using this type of coordinates. Here we summarize their most relevant features.

Working on a lined-up system, ellipsoidal coordinates ξ, η y ϕ associated to a pair of centers, A and B, lying on the Z axis are related to spherical coordinates by:

$$\xi = \frac{r_A + r_B}{R} \qquad\qquad \eta = \frac{r_A - r_B}{R} \tag{9}$$

and

$$r_A = (\xi+\eta)\frac{R}{2} \qquad r_B = (\xi-\eta)\frac{R}{2}$$

$$\text{sen}\theta_A = \frac{\sqrt{(\xi^2-1)\,(1-\eta^2)}}{(\xi+\eta)} \quad \text{sen}\theta_B = \frac{\sqrt{(\xi^2-1)\,(1-\eta^2)}}{(\xi-\eta)} \tag{10}$$

$$\cos\theta_A = \frac{\xi\eta+1}{\xi+\eta} \qquad \cos\theta_B = \frac{\xi\eta-1}{\xi-\eta}$$

It must be noticed also that:

$$x = x_A = x_B = \frac{R}{2}\,\sqrt{(\xi^2-1)\,(1-\eta^2)}\,\cos\phi \tag{11}$$

$$y = y_A = y_B = \frac{R}{2}\,\sqrt{(\xi^2-1)\,(1-\eta^2)}\,\sin\phi \tag{12}$$

$$z = z_A = \frac{R}{2}\,(\xi\,\eta+1) \tag{13}$$

$$z_B = \frac{R}{2}\,(\xi\,\eta-1) \tag{14}$$

In this system, $\phi_A = \phi_B = \phi$, and the volume element is given by:

$$d\mathbf{r} = \frac{R^3}{8}\left(\xi^2-\eta^2\right)d\eta\,d\xi\,d\phi \tag{15}$$

and the definition domain is:

$$\begin{aligned} &0 \le \phi \le 2\pi \\ &-1 \le \eta \le 1 \\ &1 \le \xi \le \infty \end{aligned} \tag{16}$$

The factor $1/|\mathbf{r}-\mathbf{r}'|$ can be expressed in terms of these coordinates as:

$$\begin{aligned} \frac{1}{|\mathbf{r}-\mathbf{r}'|} &= \left(\frac{2}{R}\right)\sum_{l=0}^{\infty}\sum_{m=0}^{l}(2-\delta_{m,0})\,(2l+1)\,\left[\frac{(l-m)!}{(l+m)!}\right]^2\,P_l^m(\xi_<)\,Q_l^m(\xi_>) \\ &\times\; P_l^m(\eta)\,P_l^m(\eta')\,\left[\cos(m\phi)\,\cos(m\phi')+\text{sen}(m\phi)\,\text{sen}(m\phi')\right] \end{aligned} \tag{17}$$

where $\xi_< = \min(\xi,\xi')$, $\xi_> = \max(\xi,\xi')$ and $P_l^m(z)$, $Q_l^m(z)$ are the corresponding Legendre functions –see [7], sección 8.7.

4 Translation of STO

Molecular integrals are specially simple if all the functions are centered at the same point of space. This fact suggests that the solution of integrals involving functions centered at different points could be simplified by referring these functions to a common center. This is the aim of the so-called *translation methods*, which are actually expansions of basis functions in regular spherical harmonics times radial factors. Placing the origin of coordinates at the common center, they read:

$$\chi^n_{LM}(\zeta, \mathbf{r}_I) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} z_l^m(\mathbf{r})\ f^I_{lm}(r) \tag{18}$$

and the several translation methods basically differ in the particular representation chosen for the radial factors.

Barnett and Coulson[12, 13] and Löwdin[14, 15] proposed more than fifty years ago to obtain the radial factors from the addition theorem of Bessel functions (Gegenbauer expansion[16]) which, when $\mathbf{R}_I$ lies on the z axis, reads:

$$\frac{e^{-\zeta r_I}}{r_I} = \sum_{l=0}^{\infty} (2l+1)\ P_l(\cos\theta)\ \frac{M_{l+1/2}(\zeta r, \zeta R_I)}{(r\, R_I)^{1/2}} \tag{19}$$

where

$$M_\nu(\zeta r, \zeta R) = I_\nu(\zeta r_<)\ K_\nu(\zeta r_>) \tag{20}$$

$r_< = \min(r, R)$, $r_> = \max(r, R)$, $P_l(\cos\theta)$ are the Legendre polynomials (see [7] seq 8.91), θ is the angle between $\mathbf{r}$ and $\mathbf{R}_I$, and $I_\nu(z)$, $K_\nu(z)$ are the corresponding Bessel functions, the latter also called Macdonald function (see [7] sec 8.4-8.5). This expression is easily extended to arbitrary $\mathbf{R}_I$ bearing in mind the addition theorem of the Legendre functions, and the result is:

$$\frac{e^{-\zeta r_I}}{r_I} = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} z_l^m(\mathbf{r})\ z_l^m(\mathbf{R}_I)\ \frac{(2l+1)\ (2-\delta_{m0})\ (l-|m|)!}{(l+|m|)!} \frac{M_{l+1/2}(\zeta r, \zeta R_I)}{(r\, R_I)^{l+1/2}} \tag{21}$$

This equation is sufficient to study the simplest integrals needed in the shift-operator context to be described in the next section but, in a different context, it must be extended to integrals involving functions with higher quantum numbers. An efficient way to carry out this task is to combine Steinborn's formula[17]:

$$-\frac{\partial}{\partial \zeta} M_\nu(\zeta r, \zeta R) = \frac{\zeta r R}{2\nu} \left[M_{\nu-1}(\zeta r, \zeta R) - M_{\nu+1}(\zeta r, \zeta R)\right] \tag{22}$$

with the recurrence relation[18]:

$$\left[r^2+R^2+\frac{(\zeta r R)^2}{2(\nu-1)(\nu+1)}\right]M_\nu(\zeta r,\zeta R)=rR\left[\frac{\nu-1}{\nu}M_{\nu-1}(\zeta r,\zeta R)+\frac{\nu+1}{\nu}M_{\nu+1}(\zeta r,\zeta R)\right]$$
$$+\quad\left(\frac{\zeta rR}{2}\right)^2\left[\frac{M_{\nu-2}(\zeta r,\zeta R)}{\nu(\nu-1)}+\frac{M_{\nu+2}(\zeta r,\zeta R)}{\nu(\nu+1)}\right] \tag{23}$$

for increasing the n quantum number and, next, to use the recurrence relations of the Legendre functions for increasing l and m. The compact results obtained in this way are illustrated with the examples of appendix 1 of ref[20].

The radial factors of eq(21) and their generalizations have different definitions for $r < R_I$ and $r > R_I$, a fact that can be unsuitable for some applications. The alternative are the one-range formulas, in particular the remarkably simple one:

$$\frac{e^{-\zeta\, r_B}}{r_B}=2\zeta\, e^{-\zeta\,(R+r)}\sum_{l=0}^{\infty}(2l+1)\;P_l(\cos\theta)\,(4\zeta^2\, r\, R)^l$$
$$\times\;\sum_{p=0}^{\infty}\frac{p!}{(p+l+1)(p+2l+1)!}\;L_p^{2l+1}(2\zeta\, r)\;L_p^{2l+1}(2\zeta\, R) \tag{24}$$

where $L_p^{2l+1}(z)$ is a Laguerre polynomial (see [7] seq 8.97). This expression, which was first derived by us[21, 22] and next studied by Steinborn[23], is valid for $\mathbf{R}_I$ lying on the z axis, but can be generalized to any orientation of $\mathbf{R}_I$ and any quantum numbers like described in the two-range case. There exist other alternatives obtained by projection of the radial functions[24, 25], but they are more complicated than eq(24) and its generalization.

5 The shift-operator technique

A very powerful tool for dealing with two-center integrals has been developed in our group[8, 9, 10], and it is based on the fact that every basis function can be obtained by applying a differential operator which acts on the real parameters of the simplest function. For STO, it gives:

$$\chi_{lm}^n(\zeta,\mathbf{r}_I)=\Omega_{lm}^n(I)\;\frac{e^{-\zeta\, r_I}}{r_I} \tag{25}$$

where

$$\Omega_{lm}^n(I)=z_l^m(\nabla_I)\;\left(-\frac{\partial}{\partial\zeta}\right)^n\;\left(-\frac{1}{\zeta}\,\frac{\partial}{\partial\zeta}\right)^l \tag{26}$$

with $\mathbf{r}_I\equiv\mathbf{r}-\mathbf{R}_I$, and $z_l^m(\nabla_I)$ being the operator obtained by replacing the corresponding cartesian coordinates by the derivatives with respect to them, in the expression of the regular harmonics in terms of these coordinates.

Note that the shift-operator of eqs(25) and (26) relate an arbitrary STO with the simplest one through parameters that remain after integration over the space variables, and therefore they also relate integrals involving arbitrary STO with those involving the simplest STO. As a consequence, integrals can be obtained in two separated steps: first, the expression of the integral involving the simplest STO is derived, and next the shift operator is applied to obtain the final integral. This approach has been applied to several types of integrals, as it will be shown later. The master formula for a two-center integral, $f_{nLM}^{n'L'M'}$, involving arbitrary quantum numbers can be derived from the basic integral, f_{000}^{000}, by:

$$\begin{aligned} f_{nLM}^{n'L'M'} &= \Omega_{LM}^{n}(I)\ \Omega_{L'M'}^{n'}(J)\ f_{000}^{000} \\ &\equiv \left(-\frac{\partial}{\partial\zeta}\right)^{n}\ \left(-\frac{\partial}{\partial\zeta'}\right)^{n'}\ z_{L}^{M}(\nabla_I)\ z_{L'}^{M'}(\nabla_J) \\ &\times \left(-\frac{1}{\zeta}\,\frac{\partial}{\partial\zeta}\right)^{L}\ \left(-\frac{1}{\zeta'}\,\frac{\partial}{\partial\zeta}\right)^{L'}\ f_{000}^{000} \end{aligned} \tag{27}$$

where the basic integral $f_{000}^{000} \equiv f(R,\zeta,\zeta')$ is the simplest of the type under consideration, i.e., that involving two $0s$ functions. In this expression, ζ and ζ' are the exponents of the $0s$ functions, and $\mathbf{R} = X\ \mathbf{i} + Y\ \mathbf{j} + Z\ \mathbf{k} \equiv (X_J - X_I)\ \mathbf{i} + (Y_J - Y_I)\ \mathbf{j} + (Z_J - Z_I)\ \mathbf{k}$.
Bearing in mind Hobson's theorem[11] and the relation:

$$\frac{\partial}{\partial X} = \frac{\partial}{\partial X_J} = -\frac{\partial}{\partial X_I} \tag{28}$$

and likewise for $\frac{\partial}{\partial Y}$ y $\frac{\partial}{\partial Z}$:

$$\begin{aligned} z_{L}^{M}(\nabla_I)\ z_{L'}^{M'}(\nabla_J)\ f(R,\zeta,\zeta') &= (-1)^{L}\ \sum_{k=0}^{L_<} \frac{2^{-k}}{k!}\ \left[\nabla^{2k}\ z_{L}^{M}(\mathbf{R})\ z_{L'}^{M'}(\mathbf{R})\right] \\ &\times \left(\frac{1}{R}\,\frac{\partial}{\partial R}\right)^{L+L'-k}\ f(R,\zeta,\zeta') \end{aligned} \tag{29}$$

where $L_< = \min(L, L')$.
Expanding in harmonics the product of regular spherical harmonics:

$$z_{L}^{M}(\mathbf{R})\ z_{L'}^{M'}(\mathbf{R}) = \sum_{l=0}^{L_<} \sum_{m} c_{L+L'-2l\,m}^{LML'M'}\ z_{L+L'-2l}^{m}(\mathbf{R})\ R^{2l} \tag{30}$$

and applying ∇^2 to both sides of the equation, the first term of 29 is attained. Applying once, it leads to:

$$\nabla^2\ z_{p}^{m}(\mathbf{R})\ R^{2l} = 4\,l\,(p+l+1/2)\ z_{p}^{m}(\mathbf{R})\ R^{2l-2} \tag{31}$$

and iterating:

$$\nabla^{2k}\ z_p^m(\mathbf{R})\ R^{2l} = \frac{2^{2k}\ l!\ \Gamma(p+l+3/2)}{(l-k)!\ \Gamma(p+l-k+3/2)}\ z_p^m(\mathbf{R})\ R^{2l-2k} \tag{32}$$

and, therefore:

$$z_L^M(\nabla_I)\ z_{L'}^{M'}(\nabla_J)\ f(R,\zeta,\zeta') = (-1)^L\ \sum_{k=0}^{L_<} \mathscr{P}_k^{LML'M'}(\mathbf{R}) \left(\frac{1}{R}\frac{\partial}{\partial R}\right)^{L+L'-k} f(R,\zeta,\zeta') \tag{33}$$

where:

$$\mathscr{P}_k^{LML'M'}(\mathbf{R}) = \frac{2^k}{k!}\ \sum_{l=k}^{L_<}\ \frac{l!\ \Gamma(L+L'-l+3/2)\ R^{2l-2k}}{(l-k)!\ \Gamma(L+L'-l-k+3/2)}\ \sum_m \alpha_{L+L'-2l\,m}^{LML'M'}\ z_{L+L'-2l}^m(\mathbf{R}) \tag{34}$$

$\alpha_{L+L'-2l\,m}^{LML'M'}$ being the expansion coefficients of the product of regular spherical harmonics in harmonics.

$$f_{nLM}^{n'L'M'} = (-1)^L\ \sum_{k=0}^{L_<} \mathscr{P}_k^{LML'M'}(\mathbf{R})\ f_k^{nL\,n'L'}(R,\zeta,\zeta') \tag{35}$$

with:

$$\begin{aligned} f_k^{nL\,n'L'}(R,\zeta,\zeta') &= \left(-\frac{\partial}{\partial\zeta}\right)^n \left(-\frac{\partial}{\partial\zeta'}\right)^{n'} \left(-\frac{1}{\zeta}\frac{\partial}{\partial\zeta}\right)^L \left(-\frac{1}{\zeta'}\frac{\partial}{\partial\zeta'}\right)^{L'} \\ &\times \left(\frac{1}{R}\frac{\partial}{\partial R}\right)^{L+L'-k} f(R,\zeta,\zeta') \end{aligned} \tag{36}$$

The presence in eq(36) of Bessel and derivative operators, which do not commute with one another, can complicate the derivation of the master formula, but this can be circumvented by using the following identities:

$$\begin{aligned} \left(-\frac{\partial}{\partial\zeta}\right)^n \left(-\frac{1}{\zeta}\frac{\partial}{\partial\zeta}\right)^L &= (-1)^{n+L}\ \zeta^n\ \sum_{i=0}^{E(n/2)} \frac{n!}{(n-2i)!\ i!\ (2\zeta^2)^i} \left(\frac{1}{\zeta}\frac{\partial}{\partial\zeta}\right)^{n-i+L} \\ &= \sum_{i=E\left[\frac{n+1}{2}\right]}^{n} \frac{n!\ (2\zeta)^{2i-n}}{(n-i)!\ (2i-n)!\ 2^i} \left(\frac{1}{\zeta}\frac{\partial}{\partial\zeta}\right)^{i+L} \end{aligned} \tag{37}$$

or

$$\left(-\frac{\partial}{\partial\zeta}\right)^n \left(-\frac{1}{\zeta}\frac{\partial}{\partial\zeta}\right)^L = \sum_{p=0}^{n+L-1} c_p^{nL} \frac{1}{\zeta^{L+p}} \left(-\frac{\partial}{\partial\zeta}\right)^{n+L-p}$$

$$= \frac{1}{\zeta^{n+2L}} \sum_{p=0}^{n+L-1} c_{n+L-1-p}^{nL} \zeta^{p+1} \left(-\frac{\partial}{\partial\zeta}\right)^{p+1} \qquad L > 0 \tag{38}$$

with

$$c_p^{nL} = (L+p-1)! \sum_i \frac{n!}{(L-i-1)!\,(n-p+i)!\,(p-i)!\,2^i\,i!} \tag{39}$$

Alternatively:

$$\left(-\frac{\partial}{\partial\zeta}\right)^n \left(-\frac{1}{\zeta}\frac{\partial}{\partial\zeta}\right)^L = \frac{1}{\zeta^{n+2L}} \sum_{p=0}^{n+L-1} c'^{nL}_p \zeta^{p+1} \left(-\frac{\partial}{\partial\zeta}\right)^{p+1} \tag{40}$$

with

$$c'^{nL}_p = (n+2L-p-2)! \sum_i \frac{n!}{(L-i-1)!\,(n-p+i)!\,(p-i)!\,2^{L-1-i}\,i!} \tag{41}$$

In both (39) and (41) the summation runs over the positive values of i for which the factorials make sense.
Obviously, the final formula and the algorithm stability will depend on the expression taken for the basic integral $f(R,\zeta,\zeta')$.

6 Two-center one-electron integrals

These integrals can be classified in three groups: two-center overlap:

$$\langle\, \chi_{LM}^n \,|\, \chi_{L'M'}^{n'} \,\rangle \equiv \int d\mathbf{r}\; \chi_{LM}^n(\zeta, \mathbf{r}_A)\; \chi_{L'M'}^{n'}(\zeta', \mathbf{r}_B) \tag{42}$$

kinetic energy:

$$\langle\, \chi_{LM}^n \,|\, -\frac{1}{2}\nabla^2 \,|\, \chi_{L'M'}^{n'} \,\rangle \equiv -\frac{1}{2}\int d\mathbf{r}\; \chi_{LM}^n(\zeta, \mathbf{r}_A)\nabla^2\chi_{L'M'}^{n'}(\zeta', \mathbf{r}_B) \tag{43}$$

and nuclear attraction integrals:

$$\langle\, \chi_{LM}^n \,|\, -\frac{Q_A}{r_A} \,|\, \chi_{L'M'}^{n'} \,\rangle \equiv -Q_A \int d\mathbf{r}\; \chi_{LM}^n(\zeta, \mathbf{r}_A)\frac{1}{r_A}\chi_{L'M'}^{n'}(\zeta', \mathbf{r}_B) \tag{44}$$

The kinetic energy and nuclear attraction integrals of eqs(43) and (44) can be easily expressed in terms of overlap integrals. In fact, since:

$$\nabla^2 \chi^{n'}_{L'M'}(\zeta', \mathbf{r}) = \zeta'^2\ \chi^{n'}_{L'M'}(\zeta', \mathbf{r}) - 2\zeta'\ (L'+n')\ \chi^{n'-1}_{L'M'}(\zeta', \mathbf{r}) + (n'-1)\ (2L'+n')\ \chi^{n'-2}_{L'M'}(\zeta', \mathbf{r}) \tag{45}$$

it follows:

$$\begin{aligned} \langle\, \chi^{n}_{LM} \,|\, -\frac{1}{2}\nabla^2 \,|\, \chi^{n'}_{L'M'} \,\rangle &= -\frac{\zeta'^2}{2} \langle\, \chi^{n}_{LM} \,|\, \chi^{n'}_{L'M'} \,\rangle + \zeta'\ (L'+n')\ \langle\, \chi^{n}_{LM} \,|\, \chi^{n'-1}_{L'M'} \,\rangle \\ &- (n'-1)\ (L'+n'/2)\ \langle\, \chi^{n}_{LM} \,|\, \chi^{n'-2}_{L'M'} \,\rangle \end{aligned} \tag{46}$$

Moreover, it is also obvious that:

$$\langle\, \chi^{n}_{LM} \,|\, -\frac{Q_A}{r_A} \,|\, \chi^{n'}_{L'M'} \,\rangle = -Q_A\ \langle\, \chi^{n-1}_{LM} \,|\, \chi^{n'}_{L'M'} \,\rangle \tag{47}$$

Clearly, the analysis of the computation of the two-center one-electron integrals can be reduced to the overlap integrals. These are, in principle, complicated functions depending on five real variables (ζ, ζ', $X_B - X_A$, $Y_B - Y_A$, $Z_B - Z_A$) and six integer quantum numbers (n, L, M, n', L', M'). However, using normalized functions and taking a lined-up axis system, they are reduced to functions of two real variables ($\zeta\ R_{AB}$, $\zeta'\ R_{AB}$) and five indices: (n, L, n', L', M) which can be further reduced to two-indices functions depending on two-variables by means of the recurrence relations of the spherical harmonics.

Simple and appealing algorithms for their calculation can be designed by reversing this process, i.e. by computing first the two-indices functions and applying next the recurrence relations to increase the quantum numbers. Notice however that there are different possible choices for this pair of indices, and every choice determines the set of recurrence relations to be applied. In principle, the best choice should lead to (i) accurate and nonexpensive two-indices functions, and (ii) a stable recursion scheme. Examples of two-indices functions fulfilling the first requirement are:

$$\langle\, \chi^{n}_{L0} \,|\, \chi^{0}_{00} \,\rangle = \int d\mathbf{r}\ z^0_L(\mathbf{r})\ r^{n-1}\ e^{-\zeta\, r}\ r_B^{-1}\ e^{-\zeta'\, r_B} \tag{48}$$

and

$$\langle\, \chi^{n}_{00} \,|\, \chi^{n'}_{00} \,\rangle = \int d\mathbf{r}\ r^{n-1}\ e^{-\zeta\, r}\ r_B^{n'-1}\ e^{-\zeta'\, r_B} \tag{49}$$

The first one, eq(48), was the choice in the first version of SMILES, in spite of the fact that the associated recursions are not stable, because that version was intended for relatively low quantum numbers, in which case the recurrence relations had to be applied a rather reduced number of times.

The second choice, eq(49), is that implemented in the current version of SMILES. It has two important features: the starting two-indices integrals can be computed with full accuracy, and the

associated recursions, though not being fully stable, downgrades more slowly than the previous one, so that moderate quantum numbers can be reached with a reasonable accuracy.
Nonetheless, as it will be shown in the next section, it is still not sufficiently good for very high quantum numbers and, therefore, we have developed a new algorithm which improves the performance of the previous ones.

6.1 Algorithm 1: the old scheme ($\langle\, \chi_{00}^{n} \,|\, \chi_{00}^{n'} \,\rangle$) scheme

The procedure starts with the two-indices integrals $\langle\, \chi_{00}^{n} \,|\, \chi_{00}^{n'} \,\rangle$ in the lined-up axis system, and next uses recurrence relations for increasing the remaining quantum numbers. The starting integrals are:

$$\langle\, \chi_{00}^{n} \,|\, \chi_{00}^{n'} \,\rangle = \int d\mathbf{r}\; r^{n-1}\; e^{-\zeta\, r}\; r_B^{n'-1}\; e^{-\zeta'\, r_B} = \left(-\frac{\partial}{\partial\zeta}\right)^{n} \left(-\frac{\partial}{\partial\zeta'}\right)^{n'} \int d\mathbf{r}\; \frac{e^{-\zeta\, r}\; e^{-\zeta'\, r_B}}{r\; r_B} \quad (50)$$

Different algorithms[1] lead to different expressions for the pending integral, and we must choose the most convenient one for taking the derivatives of eq(50) and preserving full accuracy. This is:

$$\langle\, \chi_{00}^{0} \,|\, \chi_{00}^{0} \,\rangle \equiv \int d\mathbf{r}\; \frac{e^{-\zeta\, r}\; e^{-\zeta'\, r_B}}{r\; r_B} = \frac{4\,\pi}{\zeta+\zeta'} \int_0^1 du\; e^{-\zeta\, r\, u}\; e^{-\zeta'\, R\,(1-u)} \quad (51)$$

where R is the distance AB: $R = |\mathbf{R}_B - \mathbf{R}_A| = |\mathbf{R}_B| = |Z_B|$.
Replacing (51) in (50), the derivatives can be easily taken with the aid of Leibnitz rule, leading to:

$$\begin{aligned} \langle\, \chi_{00}^{n} \,|\, \chi_{00}^{n'} \,\rangle \;\; &= \;\; 4\,\pi \sum_{p=0}^{n} \sum_{p'=0}^{n'} \binom{n}{p} \binom{n'}{p'} \frac{(n+n'-p-p')!\; R^{p+p'}}{(\zeta+\zeta')^{n+n'-p-p'+1}} \\ &\times \;\; \int_0^1 du\; u^{p}\; (1-u)^{p'}\; e^{-\zeta R u}\; e^{-\zeta' R(1-u)} \end{aligned} \quad (52)$$

or equivalently:

$$\begin{aligned} \langle\, \chi_{00}^{n} \,|\, \chi_{00}^{n'} \,\rangle = \frac{4\,\pi\; n!\; n'!\; R^{n+n'}\; e^{-\zeta R}}{\zeta+\zeta'} \sum_{k=0}^{n+n'} \frac{1}{(n+n'+1-k)!\; [(\zeta+\zeta')\, R]^{k}} \\ \times \sum_{p=\max(0,k-n)}^{\min(k,n')} \frac{k!}{(k-p)!\; p!}\; \phi\big(n'+1+p-k;\, n+n'+2-k;\, (\zeta-\zeta')/R\big) \qquad \zeta > \zeta' \end{aligned} \quad (53)$$

where $\phi(\alpha,\beta,z)$ is the confluent hypergeometric series (eq 9.210.1 of ref[7]).

Eqs(52) and (53) keep the whole accuracy if $\zeta > \zeta'$ but fail for $\zeta < \zeta'$. In this case, accuracy is recovered by means of Kummer's transformation:

$$\phi\big(\alpha, \beta, (\zeta - \zeta')\, R\big) = e^{-(\zeta' - \zeta)\, R}\, \phi\big(\beta - \alpha, \beta, (\zeta' - \zeta)\, R\big) \tag{54}$$

which simply exchanges the order in the pairs (ζ, ζ') and (n, n').
The set of recurrence relations needed for increasing the remaining quantum numbers can be easily derived from the definition ($M > 0$):

$$z_M^M(\mathbf{r}) = \frac{(M - 1/2)!}{\sqrt{\pi}}\, (2\, r\, \sin\theta)^M\, \cos M\phi \tag{55}$$

and

$$z_{L+1}^M(\mathbf{r}) = \frac{1}{L - M + 1}\, \Big[(2L + 1)\, r\, \cos\theta\, z_L^M(\mathbf{r}) - (l + M)\, r^2\, z_{L-1}^M(\mathbf{r})\Big] \tag{56}$$

with the convention: $z_L^M(\mathbf{r}) = 0$ for $L < M$.
Combination of eq(55) with the cosine theorem gives the first recurrence relation:

$$\begin{aligned}\langle\, \chi^n_{M+1M+1}\,|\,\chi^{n'}_{M+1M+1}\,\rangle = \frac{(2M+1)^2}{4R^2}\, \big[2\langle\, \chi^{n+2}_{MM}\,|\,\chi^{n'+2}_{MM}\,\rangle + 2R^2\langle\, \chi^{n+2}_{MM}\,|\,\chi^{n'}_{MM}\,\rangle \\ +\quad 2R^2\langle\, \chi^{n}_{MM}\,|\,\chi^{n'+2}_{MM}\,\rangle - \langle\, \chi^{n+4}_{MM}\,|\,\chi^{n'}_{MM}\,\rangle - \langle\, \chi^{n}_{MM}\,|\,\chi^{n'+4}_{MM}\,\rangle - R^4\langle\, \chi^{n}_{MM}\,|\,\chi^{n'}_{MM}\,\rangle\big]\end{aligned} \tag{57}$$

and eq(56) leads to:

$$\begin{aligned}\langle\, \chi^n_{L+1M}\,|\,\chi^{n'}_{L'M}\,\rangle &= \frac{2L+1}{L - |M| + 1}\, \left[\frac{\langle\, \chi^{n+2}_{LM}\,|\,\chi^{n'}_{L'M}\,\rangle + R^2\, \langle\, \chi^{n}_{LM}\,|\,\chi^{n'}_{L'M}\,\rangle - \langle\, \chi^{n}_{LM}\,|\,\chi^{n'+2}_{L'M}\,\rangle}{2\, R}\right. \\ &- \left.(L + |M|)\, \langle\, \chi^{n+2}_{L-1M}\,|\,\chi^{n'}_{L'M}\,\rangle\right]\end{aligned} \tag{58}$$

$$\begin{aligned}\langle\, \chi^n_{LM}\,|\,\chi^{n'}_{L'+1M}\,\rangle &= \frac{2L+1}{L - |M| + 1}\, \left[\frac{\langle\, \chi^{n+2}_{LM}\,|\,\chi^{n'}_{L'M}\,\rangle - R^2\, \langle\, \chi^{n}_{LM}\,|\,\chi^{n'}_{L'M}\,\rangle - \langle\, \chi^{n}_{LM}\,|\,\chi^{n'+2}_{L'M}\,\rangle}{2\, R}\right. \\ &- \left.(L + |M|)\, \langle\, \chi^{n}_{LM}\,|\,\chi^{n'+2}_{L'-1M}\,\rangle\right]\end{aligned} \tag{59}$$

The recursion scheme proceeds as it follows:

$$\begin{array}{lccccc} M = 0: & \langle\, \chi^n_{00}\,|\,\chi^{n'}_{00}\,\rangle & \xrightarrow{(58)} & \langle\, \chi^n_{L0}\,|\,\chi^{n'}_{00}\,\rangle & \xrightarrow{(59)} & \langle\, \chi^n_{L0}\,|\,\chi^{n'}_{L'0}\,\rangle \\ & \downarrow{\scriptstyle (57)} & & & & \\ M = 1: & \langle\, \chi^n_{11}\,|\,\chi^{n'}_{11}\,\rangle & \xrightarrow{(58)} & \langle\, \chi^n_{L1}\,|\,\chi^{n'}_{11}\,\rangle & \xrightarrow{(59)} & \langle\, \chi^n_{L1}\,|\,\chi^{n'}_{L'1}\,\rangle \\ & \downarrow{\scriptstyle (57)} & & & & \\ M = 2: & \ldots & & \ldots & & \ldots \end{array} \tag{60}$$

6.2 Algorithm 2: the ellipsoidal coordinates scheme

A new algorithm developed in this project is based on the formulation of the problem in ellipsoidal coordinates. This coordinates system implies working in a lined-up system as discussed in the previous section in which integrals involving funtions with different values of the M quantum number are null by symmetry. Therefore, we will consider only the case:

$$\langle \chi^n_{LM} \,|\, \chi^{n'}_{L'M} \rangle = \int d\mathbf{r}\; z^M_L(\mathbf{r}_A)\; z^M_{L'}(\mathbf{r}_B)\; r_A^{n-1}\; r_B^{n'-1}\; e^{-\zeta\, r_A}\; e^{-\zeta'\, r_B} \tag{61}$$

To express these integrals in ellipsoidal coordinates, we will separate the representation of the spherical harmonics from that of the radial factors. For these latter, it reads:

$$d\mathbf{r}\; r_A^{n-1}\; r_B^{n'-1}\; e^{-\zeta\, r_A}\; e^{-\zeta'\, r_B} = d\xi\; d\eta\; d\phi \left(\frac{R}{2}\right)^{n+n'+1} (\xi+\eta)^n\; (\xi-\eta)^{n'}\; e^{-\beta\xi}\; e^{-\nu\eta} \tag{62}$$

where $\beta = (\zeta+\zeta')\; R/2$ and $\nu = (\zeta-\zeta')\; R/2$. Expanding the binomials and grouping terms, it results:

$$d\mathbf{r}\; r_A^{n-1}\; r_B^{n'-1}\; e^{-\zeta\, r_A}\; e^{-\zeta'\, r_B} = d\xi\; d\eta\; d\phi \left(\frac{R}{2}\right)^{n+n'+1} e^{-\beta\xi}\; e^{-\nu\eta} \sum_{p=0}^{n+n'} \xi^{n+n'-p}\; \eta^p\; a_p^{nn'} \tag{63}$$

with

$$a_p^{nn'} = (-1)^p \sum_{i=\max(0,p-n')}^{\min(n,p)} \frac{n!\; n'!\; (-1)^i}{(n-i)!\; (n-p+i)!\; (p-i)!\; i!} \tag{64}$$

The coefficients $a_p^{nn'}$ can be recursively obtained by means of:

$$a_p^{n+1\,n'} = a_p^{nn'} + a_{p-1}^{nn'} \tag{65}$$

and

$$a_p^{n\,n'+1} = a_p^{nn'} - a_{p-1}^{nn'} \tag{66}$$

Eq(63) leads to:

$$\langle \chi^n_{00} \,|\, \chi^{n'}_{00} \rangle = 2\,\pi \left(\frac{R}{2}\right)^{n+n'+1} \sum_{p=0}^{n+n'} A_{n+n'-p}(\beta)\; B_p(\nu)\; a_p^{nn'} \tag{67}$$

where

$$A_j(\beta) = \int_1^\infty d\xi\; \xi^j\; e^{-\beta\,\xi} \tag{68}$$

and

$$B_j(\nu) = \int_{-1}^{1} d\eta\ \eta^j\ e^{-\nu\,\eta} \tag{69}$$

Let us consider now the expansion of the spherical harmonics. Since, $\langle\, \chi^n_{LM} \,|\, \chi^{n'}_{L'M} \,\rangle = \langle\, \chi^n_{L\,-M} \,|\, \chi^{n'}_{L'\,-M} \,\rangle$ we will consider only the case $M \geq 0$, in which:

$$\begin{aligned} z^M_L(\mathbf{r}_A)\ z^M_{L'}(\mathbf{r}_B) &= \frac{1}{2}\,(1+\cos 2M\phi)\ R^{L+L'}\ (\xi^2-1)^M\ (1-\eta^2)^M \\ &\times \frac{1}{\sqrt{\pi}} \sum_{i=0}^{E\left(\frac{L-M}{2}\right)} \frac{(L-1/2-i)!\ (-1)^i}{(L-M-2i)!\ i!\ 2^{2i}}\ (\xi\,\eta+1)^{L-M-2i}\ (\xi+\eta)^{2i} \\ &\times \frac{1}{\sqrt{\pi}} \sum_{i'=0}^{E\left(\frac{L'-M}{2}\right)} \frac{(L'-1/2-i')!\ (-1)^{i'}}{(L'-M-2i')!\ i'!\ 2^{2i'}}\ (\xi\,\eta-1)^{L'-M-2i'}\ (\xi-\eta)^{2i'} \end{aligned} \tag{70}$$

Expanding in powers of ξ and η and grouping terms, it follows:

$$z^M_L(\mathbf{r}_A)\ z^M_{L'}(\mathbf{r}_B) = \frac{1}{2}\,(1+\cos 2M\phi)\left(\frac{R}{2}\right)^{L+L'} \sum_{k=0}^{L+L'} \sum_{j=0}^{2k} \xi^{2k-j}\ \eta^j\ \alpha^{LML'M}_{kj} \tag{71}$$

Multiplying (63) by (71), the general integral can be expressed as:

$$\begin{aligned} \langle\, \chi^n_{LM} \,|\, \chi^{n'}_{L'+1M} \,\rangle &= \pi\,(1+\delta_{M0})\left(\frac{R}{2}\right)^{n+n'+L+L'+1} \sum_{k=0}^{L+L'} \sum_{j=0}^{2k} \sum_{p=0}^{n+n'} A_{n+n'+2k-j-p}(\beta) \\ &\times B_{j+p}(\nu)\ a^{nn'}_p\ \alpha^{LML'M}_{kj} \end{aligned} \tag{72}$$

or, alternatively:

$$\begin{aligned} \langle\, \chi^n_{LM} \,|\, \chi^{n'}_{L'M} \,\rangle &= \pi\,(1+\delta_{M0})\left(\frac{R}{2}\right)^{n+n'+L+L'+1} \sum_{k=0}^{L+L'} \sum_{\lambda=0}^{n+n'+2k} A_{n+n'+2k-\lambda}(\beta)\ B_\lambda(\nu) \\ &\times \sum_{j=\max(0,\lambda-n-n')}^{\min(\lambda,2k)} a^{nn'}_{\lambda-j}\ \alpha^{LML'M}_{kj} \\ &= \pi\,(1+\delta_{M0})\left(\frac{R}{2}\right)^{n+n'+L+L'+1} \sum_{k=0}^{L+L'} \sum_{\lambda=0}^{n+n'+2k} A_{n+n'+2k-\lambda}(\beta)\ B_\lambda(\nu) \\ &\times \sum_{p=\max(0,\lambda-n-n')}^{\min(\lambda,\lambda-n-n')} a^{nn'}_p\ \alpha^{LML'M}_{k\,\lambda-p} \end{aligned} \tag{73}$$

The coefficients $\alpha_{kj}^{LML'M}$ can be obtained by recursion. We start from eq(71) for the particular case $L = L' = M$:

$$\begin{aligned} z_M^M(\mathbf{r}_A)\; z_M^M(\mathbf{r}_B) &= \frac{1}{2}\,(1+\cos 2M\phi)\,\left(\frac{R}{2}\right)^{2M}\,\left[\frac{(M-1/2)!}{\sqrt{\pi}}\right]^2\,2^M\,(\xi^2-1)^M\,(1-\eta^2)^M \\ &= \frac{1}{2}\,(1+\cos 2M\phi)\,\left(\frac{R}{2}\right)^{2M}\,\left[\frac{(M-1/2)!}{\sqrt{\pi}}\right]^2\,2^M\,\sum_{k=0}^{2M}\sum_{i=0}^{2k}\xi^{2k-2j}\,\eta^{2i} \\ &\times \frac{(-1)^{k+M}\,(M!)^2}{(M+k+i)!\,(M-i)!\,(k-i)!\,i!} \end{aligned} \tag{74}$$

and define:

$$\alpha_{k\,2i+1}^{MMMM} = 0 \tag{75}$$

$$\alpha_{k\,2i}^{MMMM} = \frac{(-1)^{k+M}\,2^{2M}\,[(M-1/2)!]^2\,(M!)^2}{\pi\,(M-k+i)!\,(M-i)!\,(k-i)!\,i!} \tag{76}$$

with $0 \le i \le k$.

Next, the recurrence relation for increasing L:

$$z_{L+1}^M(\mathbf{r}) = \frac{1}{L-M+1}\,\left[(2L+1)\,\frac{R}{2}\,(1+\xi\,\eta)\,z_L^M(\mathbf{r}) - (L+M)\,\left(\frac{R}{2}\right)^2\,(\xi^2+2\,\xi\,\eta+\eta^2)\,z_{L-1}^M(\mathbf{r})\right] \tag{77}$$

leads to:

$$\begin{aligned} \alpha_{kj}^{L+1ML'M} &= \frac{2L+1}{L-M+1}\,\left(\alpha_{kj}^{LML'M} + \alpha_{k-1\,j-1}^{LML'M}\right) \\ &- \frac{L+M}{L-M+1}\,\left(\alpha_{k-1\,j}^{L-1ML'M} + 2\,\alpha_{k-1\,j-1}^{L-1ML'M} + \alpha_{k-1\,j-2}^{L-1ML'M}\right) \end{aligned} \tag{78}$$

where $z_{M-1}^M(\mathbf{r}) = 0$.

For increasing L':

$$z_{L'+1}^M(\mathbf{r}) = \frac{1}{L'-M+1}\,\left[-(2L'+1)\,\frac{R}{2}\,(1-\xi\,\eta)\,z_{L'}^M(\mathbf{r}) - (L'+M)\,\left(\frac{R}{2}\right)^2\,(\xi^2-2\,\xi\,\eta+\eta^2)\,z_{L'-1}^M(\mathbf{r})\right] \tag{79}$$

leads to:

$$\begin{aligned} \alpha_{kj}^{LM\,L'+1M} &= -\frac{2L'+1}{L'-M+1}\,\left(\alpha_{kj}^{LML'M} - \alpha_{k-1\,j-1}^{LML'M}\right) \\ &- \frac{L'+M}{L'-M+1}\,\left(\alpha_{k-1\,j}^{LM\,L'-1M} - 2\,\alpha_{k-1\,j-1}^{LM\,L'-1M} + \alpha_{k-1\,j-2}^{LM\,L'-1M}\right) \end{aligned} \tag{80}$$

6.3 Tests on the accuracy of algorithms 1 and 2

The first test illustrates the accuracy of the two above described algorithms in case of moderate quantum numbers. Fig 1 gives the order of magnitude of the integrals involving normalized STO for a range of exponents and with quantum numbers: $N_A = N_B = 10$, $L_A = L_B = 5$, and $-5 \leq M \leq 5$. Notice that, in the notation used throughout this report: $n = N - L$, i.e., the integrals correspond to $n_A = n_B = 5$ in this notation. The scaled exponents ($\overline{\zeta}_A \equiv \zeta_A \; R$, $\overline{\zeta}_B \equiv \zeta_B \; R$) range from $5 \cdot 10^{-3}$ to $5 \cdot 10^{2}$ in an almost exponential way.

Integrals $n_A=n_B=5;\ \ l_A=l_B=5;\ R = 1$

Overlap integrals with normalized STO: $n_A=n_B=5,\ l_A=l_B=5,\ R = 1$

Decimal logarithm of the absolute value of the integrals

Exps	0.005	0.01	0.03	0.06	0.12	0.25	0.5	1	2	4	8	16	32	64	128	256	512
0.005	0	-1	-3	-6	-9	-12	-15	-18	-21	-24	-27	-29	-31	-33	-35	-37	-39
0.01	-1	0	-1	-3	-6	-9	-12	-15	-18	-21	-24	-26	-28	-30	-32	-34	-36
0.03	-3	-1	0	-1	-2	-4	-7	-10	-13	-16	-19	-21	-23	-25	-27	-29	-31
0.06	-6	-3	-1	0	-1	-2	-4	-7	-10	-13	-15	-18	-20	-22	-24	-26	-28
0.12	-9	-6	-2	-1	0	-1	-2	-4	-7	-10	-12	-15	-17	-19	-21	-23	-25
0.25	-12	-9	-4	-2	-1	0	-1	-2	-4	-7	-9	-11	-14	-16	-18	-20	-21
0.5	-15	-12	-7	-4	-2	-1	0	-1	-2	-4	-6	-9	-11	-13	-15	-17	-19
1	-18	-15	-10	-7	-4	-2	-1	0	-1	-2	-4	-6	-8	-10	-12	-14	-16
2	-21	-18	-13	-10	-7	-4	-2	-1	0	-1	-2	-4	-6	-8	-10	-12	-14
4	-24	-21	-16	-13	-10	-7	-4	-2	-1	0	-1	-2	-4	-6	-8	-10	-12
8	-27	-24	-19	-15	-12	-9	-6	-4	-2	-1	-1	-1	-3	-4	-6	-8	-10
16	-29	-26	-21	-18	-15	-11	-9	-6	-4	-2	-1	-1	-1	-3	-5	-7	-9
32	-31	-28	-23	-20	-17	-14	-11	-8	-6	-4	-3	-1	-2	-4	-6	-8	-10
64	-33	-30	-25	-22	-19	-16	-13	-10	-8	-6	-4	-3	-4	-10	-15	-17	-19
128	-35	-32	-27	-24	-21	-18	-15	-12	-10	-8	-6	-5	-6	-15	-31	-39	-42
256	-37	-34	-29	-26	-23	-20	-17	-14	-12	-10	-8	-7	-8	-17	-39	-81	-92
512	-39	-36	-31	-28	-25	-21	-19	-16	-14	-12	-10	-9	-10	-19	-42	-92	-186

Figure 1: Overlap integrals with $N_A = N_B = 10$, $L_A = L_B = 5$

Region of exponents corresponding to negligible integrals (absolute value lower than 10^{-15}) is coloured in this and the following figures. The behavior of the algorithms in this region is rather irrelevant, but we have kept the values attained therein to fully illustrate the analysis carried out. It must be recalled that the information on the number of absolute *decimal* figures in this region can be completely useless: for very small integrals, there can be a high number of accurate decimal figures (zeroes) even in cases in which the order of magnitude in the computed integral is wrong.

The figure shows that these integrals have meaningful values even for relatively large scaled

exponents (in the range of 30).

The number of correct *significant* figures (i.e. the relative error) attained with both algorithms working in double precision are reported in figure 2. In this case as well as in the remaining tables, the reference values were computed with the algorithm based in ellipsoidal coordinates using multiprecision (65 significant digits in computation). A previous analysis on the consistence of the results was made using different working precision values (lower and higher that those finally chosen) in a number of selected cases. This analysis showed that the number of digits finally taken in the calculations was sufficient to yield more than 20 correct significant figures in the results for all the selected range of exponents. Figure 3 gives the number of correct *decimal* places (absolute error).

Integrals $n_A=n_B=5;\ \ l_A=l_B=5;\ R = 1$

Algorithm based on recursion over L,L' and M starting from integrals <N00|N'00>

Number of accurate significant figures of integrals computed in double precision

Exps	0.005	0.01	0.03	0.06	0.12	0.25	0.5	1	2	4	8	16	32	64	128	256	512
0.005	0	0	0	0	0	0	0	0	2	6	8	10	10	7	5	2	0
0.01	0	0	0	0	0	0	0	0	2	5	9	10	10	8	4	2	0
0.03	0	0	0	0	0	0	0	0	2	5	8	10	10	8	5	2	0
0.06	0	0	0	0	0	0	0	0	3	5	8	10	10	8	5	2	0
0.12	0	0	0	0	0	0	0	0	3	6	8	10	10	8	5	2	0
0.25	0	0	0	0	0	0	0	0	3	7	9	10	10	8	5	1	0
0.5	0	0	0	0	0	0	0	1	3	6	9	11	10	7	4	2	0
1	0	0	0	0	0	0	1	3	4	6	9	10	9	7	5	1	0
2	2	2	2	3	3	3	3	4	5	6	8	10	10	6	4	1	0
4	6	5	5	5	6	7	6	6	6	7	9	11	10	7	3	0	0
8	8	8	8	8	8	9	9	9	8	9	10	8	9	6	3	0	0
16	10	10	10	10	10	10	11	10	10	11	8	13	11	8	5	2	0
32	10	10	10	10	10	10	11	10	10	10	10	11	11	8	5	2	0
64	7	8	8	8	8	8	8	8	7	7	7	9	8	9	5	2	0
128	5	4	5	5	5	5	5	5	5	3	3	5	5	5	7	2	0
256	2	2	2	2	2	1	2	2	1	1	0	2	2	2	2	6	0
512	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	4

Integrals $n_A=n_B=5;\ \ l_A=l_B=5;\ R = 1$

Algorithm based on ellipsoidal coordinates

Number of accurate significant figures of integrals computed in double precision

Exps	0.005	0.01	0.03	0.06	0.12	0.25	0.5	1	2	4	8	16	32	64	128	256	512
0.005	14	14	14	14	13	13	13	13	13	13	13	12	7	4	0	0	0
0.01	14	14	13	14	14	13	14	14	13	14	13	12	7	4	0	0	0
0.03	14	13	13	13	13	13	14	13	13	14	13	11	7	5	0	0	0
0.06	14	14	13	13	13	14	13	14	14	13	13	12	7	4	0	0	0
0.12	13	14	13	13	13	13	13	13	13	14	13	12	8	4	0	0	0
0.25	13	13	13	14	13	14	14	13	14	13	13	11	8	5	0	0	0
0.5	13	14	14	13	13	14	14	13	14	13	13	11	8	5	0	0	0
1	13	14	13	14	13	13	13	14	14	13	13	11	8	4	0	0	0
2	13	13	13	14	13	14	14	14	13	13	12	11	8	4	0	0	0
4	13	13	13	13	14	13	13	13	13	13	12	11	8	3	0	0	0
8	13	13	13	13	13	13	13	13	12	12	13	8	7	3	0	0	0
16	12	12	11	12	12	11	12	11	11	11	8	12	9	4	0	0	0
32	7	7	7	7	8	8	8	8	8	8	7	9	10	6	0	0	0
64	5	5	5	4	4	5	4	4	4	3	2	4	6	9	0	0	0
128	0	0	0	0	0	0	0	0	0	0	0	0	0	2	6	0	0
256	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	4	0
512	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	3

Figure 2: Accurate significant figures in double precision for overlap integrals with $N_A = N_B = 10$, $L_A = L_B = 5$

Integrals $n_A=n_B=5;\ \ l_A=l_B=5;\ R=1$

Algorithm based on recursion over L,L' and M starting from integrals <N00|N'00>

Number of accurate decimal figures of integrals computed in double precision

Exps	0.005	0.01	0.03	0.06	0.12	0.25	0.5	1	2	4	8	16	32	64	128	256	512
0.005	0	0	0	0	0	6	11	18	23	30	35	39	41	41	40	39	39
0.01	0	0	0	0	0	2	9	14	20	26	32	36	38	38	38	36	34
0.03	0	0	0	0	0	0	3	10	15	21	27	31	33	34	32	31	30
0.06	0	0	0	0	0	0	1	7	12	18	24	28	30	30	29	29	27
0.12	0	0	0	0	0	0	0	4	10	15	20	25	27	26	26	24	24
0.25	6	2	0	0	0	0	0	2	7	14	18	22	24	23	22	21	20
0.5	11	9	3	1	0	0	0	1	5	10	15	19	20	20	19	19	17
1	18	14	10	7	4	2	1	3	5	8	13	17	17	17	17	16	15
2	23	20	15	12	10	7	5	5	5	7	10	14	16	14	14	13	12
4	30	26	21	18	15	13	10	8	7	8	10	13	14	13	11	10	10
8	35	32	27	24	20	18	15	13	10	10	11	13	12	11	10	9	8
16	39	36	31	28	25	22	19	17	14	13	12	13	12	11	10	9	8
32	41	40	33	30	27	24	21	18	16	14	13	13	15	15	14	13	12
64	41	38	33	30	27	24	21	18	15	13	13	12	15	23	24	24	23
128	40	37	32	29	27	23	20	17	15	11	11	11	14	25	44	48	47
256	39	36	31	28	25	22	19	16	13	11	9	10	13	24	48	94	100
512	39	35	30	28	24	21	17	15	12	9	8	8	12	23	48	99	200

Integrals $n_A=n_B=5;\ \ l_A=l_B=5;\ R=1$

Algorithm based on ellipsoidal coordinates

Number of accurate decimal figures of integrals computed in double precision

Exps	0.005	0.01	0.03	0.06	0.12	0.25	0.5	1	2	4	8	16	32	64	128	256	512
0.005	14	14	17	20	22	25	28	31	34	37	40	41	39	38	36	33	31
0.01	14	14	15	17	19	22	26	28	31	34	37	38	36	35	32	30	27
0.03	17	15	13	14	16	18	21	24	26	29	31	32	31	30	27	24	22
0.06	20	17	14	13	14	16	18	21	24	26	28	30	27	27	25	22	19
0.12	22	19	16	14	13	14	16	18	20	24	26	26	24	24	21	19	16
0.25	25	22	18	16	14	14	14	16	18	20	23	23	21	20	18	15	13
0.5	28	26	21	18	16	14	14	14	16	18	20	20	18	17	15	12	10
1	31	28	24	21	18	16	14	14	14	16	17	17	16	14	12	10	6
2	34	31	26	24	20	18	16	14	14	14	15	15	13	12	9	6	4
4	37	34	29	26	24	20	18	15	14	14	14	13	12	9	7	4	2
8	40	37	31	28	26	22	20	17	15	14	14	13	10	8	5	3	0
16	41	38	32	30	26	23	20	17	15	13	13	13	10	8	6	3	1
32	39	36	31	27	24	21	18	16	13	12	10	10	14	11	10	7	4
64	39	35	30	27	23	20	17	14	12	9	8	8	11	22	21	18	15
128	36	32	27	24	21	18	15	12	9	7	6	6	10	20	44	42	40
256	33	30	24	22	19	15	12	9	6	4	3	3	7	18	42	94	92
512	31	27	22	19	16	13	10	7	4	2	0	1	4	15	40	92	198

Figure 3: Accurate decimal figures in double precision for overlap integrals with $N_A = N_B = 10$, $L_A = L_B = 5$

Integrals $n_A=n_B=5;\ \ l_A=l_B=5;\ R=1$

Algorithm based on recursion over L,L' and M starting from integrals <N00|N'00>

Number of accurate significant figures of integrals computed in quadruple precision

Exps	0.005	0.01	0.03	0.06	0.12	0.25	0.5	1	2	4	8	16	32	64	128	256	512
0.005	0	0	3	5	8	11	14	18	20	23	26	28	28	26	23	20	17
0.01	0	0	3	6	8	12	15	18	21	23	26	29	28	26	23	20	17
0.03	3	3	6	7	9	12	15	17	21	24	26	29	29	26	23	20	17
0.06	5	7	8	8	10	12	15	17	20	23	27	29	28	26	23	20	17
0.12	9	9	9	10	11	13	16	18	21	24	26	29	28	26	23	20	17
0.25	11	12	12	13	13	14	16	19	21	23	27	28	28	26	23	20	17
0.5	15	15	15	15	16	16	17	19	21	24	26	29	28	26	22	19	17
1	18	18	17	17	19	18	19	20	22	24	26	28	28	25	22	19	17
2	20	21	21	21	21	21	21	22	23	25	27	28	27	25	22	19	16
4	23	23	24	23	24	24	24	25	25	25	28	28	27	24	22	19	16
8	26	26	26	27	26	27	26	26	27	28	28	26	27	25	21	18	15
16	28	29	29	29	29	29	29	28	29	28	26	30	29	26	23	20	17
32	28	28	29	28	28	28	28	28	28	27	27	29	30	27	23	20	17
64	26	26	26	26	26	26	26	26	25	25	25	26	27	28	25	20	17
128	23	23	23	24	23	23	23	23	22	22	21	23	23	25	26	21	17
256	20	20	20	20	20	20	20	20	19	19	18	20	20	20	21	24	17
512	17	17	17	17	17	17	17	17	16	16	15	17	17	17	16	17	23

Integrals $n_A=n_B=5;\ \ l_A=l_B=5;\ R=1$

Algorithm based on ellipsoidal coordinates

Number of accurate significant figures of integrals computed in quadruple precision

Exps	0.005	0.01	0.03	0.06	0.12	0.25	0.5	1	2	4	8	16	32	64	128	256	512
0.005	32	31	31	32	31	31	32	32	32	31	31	30	25	23	18	13	9
0.01	31	32	32	32	31	31	31	32	32	31	31	29	25	23	18	13	9
0.03	31	32	32	31	31	31	32	32	31	31	31	30	25	22	18	13	9
0.06	32	32	31	32	31	31	32	32	31	31	31	30	25	22	18	13	9
0.12	31	31	31	31	31	31	31	32	31	32	31	29	25	23	18	13	9
0.25	31	31	31	31	32	32	32	32	32	31	31	30	25	22	18	13	9
0.5	32	31	32	32	31	32	32	31	32	31	31	30	25	22	18	13	9
1	32	32	32	32	32	32	31	31	31	31	30	30	26	22	18	13	9
2	32	32	31	31	31	32	32	31	32	31	31	29	26	22	17	13	8
4	31	31	31	31	32	32	31	31	31	30	30	29	25	21	17	12	8
8	31	31	31	31	31	31	31	30	31	30	31	26	25	20	16	12	7
16	30	30	30	30	29	30	30	30	29	29	26	30	27	22	18	13	9
32	25	25	25	25	25	25	25	26	26	25	25	27	28	24	19	14	9
64	23	23	22	22	23	22	23	22	22	21	21	23	24	26	19	14	9
128	18	18	18	18	18	18	18	18	17	17	16	18	18	19	24	15	9
256	13	13	13	13	13	13	13	13	13	12	11	14	13	14	15	23	10
512	9	9	9	9	9	9	9	9	9	8	7	9	9	9	10	10	22

Figure 4: Accurate significant figures in quadruple precision for overlap integrals with $N_A = N_B = 10$, $L_A = L_B = 5$

Integrals $n_A=n_B=5;\ \ l_A=l_B=5;\ R=1$

Algorithm based on recursion over L,L' and M starting from integrals <N00|N'00>

Number of accurate decimal figures of integrals computed in quadruple precision

Exps	0.005	0.01	0.03	0.06	0.12	0.25	0.5	1	2	4	8	16	32	64	128	256	512
0.005	0	0	6	11	17	23	29	35	41	47	53	58	60	59	58	58	56
0.01	0	0	5	9	14	21	27	33	39	44	50	55	56	56	56	54	53
0.03	6	5	6	8	11	16	22	27	34	40	45	50	52	51	50	49	48
0.06	11	10	8	8	10	14	19	24	30	36	42	47	48	47	47	46	45
0.12	18	14	11	10	11	14	18	23	28	33	39	43	45	45	44	42	42
0.25	23	21	16	15	14	14	16	21	25	30	36	40	42	42	41	39	38
0.5	29	26	22	19	18	16	17	19	24	28	33	38	39	39	37	36	35
1	35	32	27	24	23	20	19	21	22	27	30	34	36	35	34	33	33
2	41	39	34	31	28	25	23	22	23	26	29	32	33	33	32	31	30
4	47	44	40	36	33	30	28	27	26	26	29	31	32	30	30	29	28
8	53	50	45	42	39	36	33	30	30	29	29	30	30	30	28	27	26
16	57	55	50	46	44	40	37	34	33	31	30	31	30	29	29	27	26
32	60	56	52	48	45	42	39	36	33	32	30	31	33	33	32	31	30
64	59	56	52	49	45	41	39	35	33	30	30	30	33	41	43	41	42
128	59	56	51	48	44	40	38	35	32	30	28	29	33	43	62	65	66
256	57	54	49	46	43	40	37	34	31	29	27	27	32	42	66	112	117
512	56	53	48	45	42	39	36	33	30	28	26	27	30	41	65	117	217

Integrals $n_A=n_B=5;\ \ l_A=l_B=5;\ R=1$

Algorithm based on ellipsoidal coordinates

Number of accurate decimal figures of integrals computed in quadruple precision

Exps	0.005	0.01	0.03	0.06	0.12	0.25	0.5	1	2	4	8	16	32	64	128	256	512
0.005	32	32	35	38	40	43	47	50	53	56	57	60	56	57	54	51	49
0.01	32	32	34	35	37	40	43	46	50	52	54	56	53	53	51	48	45
0.03	35	33	32	32	33	36	39	42	44	47	50	51	48	48	46	43	40
0.06	38	35	32	32	32	34	36	39	42	44	47	48	45	45	43	40	37
0.12	40	37	33	32	32	32	34	36	38	42	43	44	42	42	39	37	34
0.25	43	40	36	34	33	32	32	34	36	38	40	41	39	38	36	33	31
0.5	47	43	39	36	34	32	32	32	34	35	37	38	36	35	33	30	28
1	50	46	42	39	36	34	32	32	32	33	35	36	34	32	30	27	24
2	53	50	44	42	38	36	34	32	32	32	33	33	32	30	27	25	22
4	56	52	47	44	42	39	35	33	32	31	32	32	30	27	25	22	20
8	57	54	50	46	43	40	37	35	33	32	32	31	29	26	24	21	18
16	60	56	51	48	44	41	38	36	33	32	31	31	29	26	24	21	19
32	56	53	48	45	42	39	36	34	32	30	29	29	32	29	27	25	23
64	57	53	48	45	42	39	35	32	30	27	26	26	29	41	38	36	33
128	54	51	46	43	39	36	33	30	27	25	24	24	27	38	62	60	58
256	51	48	43	40	37	33	30	28	25	22	21	21	25	36	60	112	110
512	49	45	40	37	34	31	28	24	22	20	18	19	23	33	58	110	217

Figure 5: Accurate decimal figures in quadruple precision for overlap integrals with $N_A = N_B = 10$, $L_A = L_B = 5$

Integrals $n_A=n_B=10;\ \ l_A=l_B=10;\ R = 1$

Overlap integrals with normalized STO: $n_A=n_B=10,\ l_A=l_B=10,\ R = 1$

Decimal logarithm of the absolute value of the integrals

Exps	0.005	0.01	0.03	0.06	0.12	0.25	0.5	1	2	4	8	16	32	64	128	256	512
0.005	0	-1	-6	-11	-17	-23	-29	-35	-41	-47	-53	-58	-62	-66	-70	-73	-77
0.01	-1	0	-3	-6	-11	-17	-23	-29	-35	-41	-46	-52	-56	-60	-64	-67	-70
0.03	-6	-3	0	-1	-4	-9	-14	-19	-25	-31	-37	-42	-46	-50	-54	-57	-61
0.06	-11	-6	-1	0	-1	-4	-9	-14	-19	-25	-31	-36	-40	-44	-48	-51	-55
0.12	-17	-11	-4	-1	0	-1	-4	-9	-14	-19	-25	-30	-34	-38	-41	-45	-48
0.25	-23	-17	-9	-4	-1	0	-1	-4	-8	-13	-18	-23	-28	-31	-35	-39	-42
0.5	-29	-23	-14	-9	-4	-1	0	-1	-4	-8	-13	-17	-22	-26	-29	-33	-36
1	-35	-29	-19	-14	-9	-4	-1	0	-1	-4	-8	-12	-16	-20	-23	-27	-30
2	-41	-35	-25	-19	-14	-8	-4	-1	0	-1	-4	-7	-11	-14	-18	-21	-25
4	-47	-41	-31	-25	-19	-13	-8	-4	-1	0	-1	-4	-7	-11	-14	-17	-21
8	-53	-46	-37	-31	-25	-18	-13	-8	-4	-1	0	-2	-4	-7	-11	-14	-17
16	-58	-52	-42	-36	-30	-23	-17	-12	-7	-4	-2	-1	-2	-4	-7	-11	-14
32	-62	-56	-46	-40	-34	-28	-22	-16	-11	-7	-4	-2	-1	-2	-5	-8	-11
64	-66	-60	-50	-44	-38	-31	-26	-20	-14	-11	-7	-4	-2	-3	-8	-12	-15
128	-70	-64	-54	-48	-41	-35	-29	-23	-18	-14	-11	-7	-5	-8	-19	-28	-33
256	-73	-67	-57	-51	-45	-39	-33	-27	-21	-17	-14	-11	-8	-12	-28	-62	-77
512	-77	-70	-61	-55	-48	-42	-36	-30	-25	-21	-17	-14	-11	-15	-33	-77	-161

Figure 6: Overlap integrals with $N_A = N_B = 20$, $L_A = L_B = 10$

Integrals $n_A=n_B=10;\ l_A=l_B=10;\ R = 1$

Algorithm based on recursion over L,L' and M starting from integrals <N00|N'00>

Number of accurate significant figures of integrals computed in double precision

Exps	0.005	0.01	0.03	0.06	0.12	0.25	0.5	1	2	4	8	16	32	64	128	256	512
0.005	0	0	0	0	0	0	0	0	0	0	0	0	5	4	0	0	0
0.01	0	0	0	0	0	0	0	0	0	0	0	0	4	3	0	0	0
0.03	0	0	0	0	0	0	0	0	0	0	0	0	4	4	0	0	0
0.06	0	0	0	0	0	0	0	0	0	0	0	0	4	3	0	0	0
0.12	0	0	0	0	0	0	0	0	0	0	0	0	4	4	0	0	0
0.25	0	0	0	0	0	0	0	0	0	0	0	0	4	4	0	0	0
0.5	0	0	0	0	0	0	0	0	0	0	0	0	3	4	0	0	0
1	0	0	0	0	0	0	0	0	0	0	0	0	4	3	0	0	0
2	0	0	0	0	0	0	0	0	0	0	0	0	4	3	0	0	0
4	0	0	0	0	0	0	0	0	0	0	0	0	3	2	0	0	0
8	0	0	0	0	0	0	0	0	0	0	0	2	3	1	0	0	0
16	0	0	0	0	0	0	0	0	0	0	2	5	6	1	0	0	0
32	4	4	4	4	4	4	3	4	4	3	3	6	9	5	0	0	0
64	4	4	4	4	4	4	4	4	4	2	1	1	5	6	0	0	0
128	0	0	0	0	0	0	0	0	0	0	0	0	0	0	2	0	0
256	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
512	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

Integrals $n_A=n_B=10;\ l_A=l_B=10;\ R = 1$

Algorithm based on ellipsoidal coordinates

Number of accurate significant figures of integrals computed in double precision

Exps	0.005	0.01	0.03	0.06	0.12	0.25	0.5	1	2	4	8	16	32	64	128	256	512
0.005	10	10	10	10	10	10	10	10	10	10	9	9	6	0	0	0	0
0.01	10	10	10	10	10	10	10	10	10	10	9	9	7	0	0	0	0
0.03	10	10	10	10	10	10	10	10	10	10	9	9	7	0	0	0	0
0.06	10	10	10	10	10	10	10	10	10	10	9	9	6	0	0	0	0
0.12	10	10	10	10	10	10	10	10	10	10	10	9	7	0	0	0	0
0.25	10	10	10	10	10	10	10	10	10	10	10	8	7	0	0	0	0
0.5	10	10	10	10	10	10	10	10	10	10	9	9	7	0	0	0	0
1	10	10	10	10	10	10	10	10	10	9	9	9	6	0	0	0	0
2	10	10	10	10	10	10	10	10	11	9	9	8	6	0	0	0	0
4	10	10	10	10	10	10	10	10	9	9	8	6	5	0	0	0	0
8	9	9	9	9	10	10	9	9	9	8	10	7	3	0	0	0	0
16	9	8	9	8	9	9	9	9	8	6	7	8	4	0	0	0	0
32	6	7	6	6	7	6	6	6	6	5	3	4	6	0	0	0	0
64	0	0	0	0	0	0	0	0	0	0	0	0	0	3	0	0	0
128	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
256	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
512	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

Figure 7: Accurate significant figures in double precision for overlap integrals with $N_A = N_B = 20$, $L_A = L_B = 10$

Integrals $n_A=n_B=10;\ \ l_A=l_B=10;\ R=1$

Algorithm based on recursion over L,L' and M starting from integrals <N00|N'00>

Number of accurate decimal figures of integrals computed in double precision

Exps	0.005	0.01	0.03	0.06	0.12	0.25	0.5	1	2	4	8	16	32	64	128	256	512
0.005	0	0	0	0	0	0	0	11	23	35	47	57	67	70	69	68	65
0.01	0	0	0	0	0	0	0	5	17	30	41	51	60	63	63	61	59
0.03	0	0	0	0	0	0	0	0	8	20	31	42	50	55	53	51	49
0.06	0	0	0	0	0	0	0	0	2	14	25	35	44	47	47	45	42
0.12	0	0	0	0	0	0	0	0	0	9	19	30	38	42	41	39	37
0.25	0	0	0	0	0	0	0	0	0	3	13	24	32	35	34	33	30
0.5	0	0	0	0	0	0	0	0	0	0	7	17	25	30	28	27	24
1	11	5	0	0	0	0	0	0	0	0	3	12	21	23	22	20	19
2	23	17	8	2	0	0	0	0	0	0	0	8	15	18	17	14	12
4	35	30	20	14	9	3	0	0	0	0	0	5	11	12	11	9	6
8	47	41	31	25	19	13	7	3	0	0	0	5	8	9	7	5	3
16	57	51	42	35	30	24	17	12	8	5	5	7	8	7	4	2	0
32	67	60	50	44	38	32	25	21	15	11	8	8	10	8	6	3	0
64	70	64	54	48	42	35	30	24	18	13	9	7	8	12	13	11	8
128	69	63	53	48	41	35	28	23	17	12	8	5	7	13	29	31	29
256	69	61	51	45	40	33	27	20	15	9	6	3	4	12	31	73	77
512	65	59	49	43	37	30	24	18	12	7	3	0	1	9	30	78	172

Integrals $n_A=n_B=10;\ \ l_A=l_B=10;\ R=1$

Algorithm based on ellipsoidal coordinates

Number of accurate decimal figures of integrals computed in double precision

Exps	0.005	0.01	0.03	0.06	0.12	0.25	0.5	1	2	4	8	16	32	64	128	256	512
0.005	10	11	16	21	27	33	39	45	51	57	62	67	68	61	61	55	50
0.01	11	11	13	17	22	27	33	39	45	51	56	60	63	55	55	49	44
0.03	16	13	10	11	14	19	24	29	35	41	46	50	53	46	45	40	34
0.06	21	17	11	10	11	14	19	24	29	35	40	44	47	39	39	33	28
0.12	27	22	14	11	10	11	14	19	24	29	34	38	41	33	33	27	22
0.25	33	27	19	14	11	11	11	14	18	23	28	32	34	27	26	21	15
0.5	39	33	24	19	14	11	11	11	14	18	22	26	29	21	20	15	9
1	45	39	29	24	19	14	11	11	11	13	17	21	23	15	14	9	3
2	51	45	35	29	24	18	14	11	11	11	14	16	17	10	9	3	0
4	57	51	41	35	29	23	18	14	11	11	10	12	12	6	4	0	0
8	62	56	46	40	34	28	22	17	14	11	11	10	9	3	0	0	0
16	67	60	50	44	38	32	26	21	16	12	10	10	7	2	0	0	0
32	68	63	53	47	41	34	28	23	17	12	8	6	8	3	0	0	0
64	61	55	46	39	33	27	21	15	10	6	3	2	2	10	2	0	0
128	61	54	45	39	33	26	21	14	8	3	0	0	0	2	26	21	15
256	55	49	39	33	27	21	15	9	3	0	0	0	0	0	20	69	65
512	50	44	34	28	22	15	9	3	0	0	0	0	0	0	15	65	169

Figure 8: Accurate decimal figures in double precision for overlap integrals with $N_A = N_B = 20$, $L_A = L_B = 10$

Integrals $n_A=n_B=10;\ l_A=l_B=10;\ R=1$

Algorithm based on recursion over L,L' and M starting from integrals <N00|N'00>

Number of accurate significant figures of integrals computed in quadruple precision

Exps	0.005	0.01	0.03	0.06	0.12	0.25	0.5	1	2	4	8	16	32	64	128	256	512
0.005	0	0	0	0	0	0	0	0	0	6	12	18	22	22	17	12	6
0.01	0	0	0	0	0	0	0	0	0	6	12	18	22	22	17	12	6
0.03	0	0	0	0	0	0	0	0	1	6	12	18	22	22	17	12	6
0.06	0	0	0	0	0	0	0	0	0	7	13	18	22	22	17	12	5
0.12	0	0	0	0	0	0	0	0	1	6	12	18	22	22	17	12	6
0.25	0	0	0	0	0	0	0	0	2	7	12	18	22	22	17	11	5
0.5	0	0	0	0	0	0	0	0	2	8	13	18	22	22	17	11	6
1	0	0	0	0	0	0	0	1	4	9	13	18	22	22	17	11	5
2	0	0	1	0	1	2	2	4	7	9	14	18	22	21	17	11	5
4	6	6	6	7	6	7	8	9	9	11	15	17	21	20	16	10	4
8	12	12	12	13	12	12	13	13	14	15	18	20	20	20	14	8	3
16	18	18	18	18	18	18	18	18	18	17	20	22	23	19	15	8	3
32	22	22	22	22	22	22	22	22	22	21	20	23	27	23	18	12	5
64	22	22	22	22	22	22	22	22	21	20	20	19	23	25	17	12	6
128	17	17	17	17	17	17	17	17	17	16	14	15	18	17	20	12	5
256	12	12	12	11	12	12	11	12	12	10	8	9	12	12	12	17	6
512	6	6	6	5	6	5	6	5	6	4	3	3	5	6	6	6	14

Integrals $n_A=n_B=10;\ l_A=l_B=10;\ R=1$

Algorithm based on ellipsoidal coordinates

Number of accurate significant figures of integrals computed in quadruple precision

Exps	0.005	0.01	0.03	0.06	0.12	0.25	0.5	1	2	4	8	16	32	64	128	256	512
0.005	28	28	28	28	28	28	28	28	28	28	27	27	24	14	8	0	0
0.01	28	28	28	28	28	28	28	28	28	28	28	26	24	14	9	0	0
0.03	28	28	28	28	28	28	28	28	28	28	28	27	25	14	8	0	0
0.06	28	28	28	28	28	28	28	28	28	28	27	27	25	14	8	0	0
0.12	28	28	28	28	28	28	29	28	28	28	27	27	25	14	9	0	0
0.25	28	28	28	28	28	28	28	28	28	28	27	27	25	14	8	0	0
0.5	28	28	28	28	29	28	28	28	28	28	27	26	24	14	8	0	0
1	28	28	28	28	28	28	28	28	28	28	28	27	24	14	9	0	0
2	28	28	28	28	28	28	28	28	28	28	27	26	24	13	8	0	0
4	28	28	28	28	28	28	28	28	28	28	27	24	23	13	7	0	0
8	27	28	28	28	27	27	27	28	27	27	28	25	21	14	6	0	0
16	27	27	27	27	27	27	26	27	26	24	25	25	22	14	5	0	0
32	25	24	25	25	25	25	24	24	24	23	21	22	25	18	8	0	0
64	14	14	14	14	14	14	14	14	13	13	14	14	18	21	9	0	0
128	8	9	8	8	9	8	8	9	9	7	6	5	8	9	16	1	0
256	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	12	0
512	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	9

Figure 9: Accurate significant figures in quadruple precision for overlap integrals with $N_A = N_B = 20$, $L_A = L_B = 10$

Integrals $n_A=n_B=10;\ l_A=l_B=10;\ R=1$

Algorithm based on recursion over L,L' and M starting from integrals <N00|N'00>

Number of accurate decimal figures of integrals computed in quadruple precision

Exps	0.005	0.01	0.03	0.06	0.12	0.25	0.5	1	2	4	8	16	32	64	128	256	512
0.005	0	0	0	0	0	5	17	29	41	53	65	76	85	88	87	85	82
0.01	0	0	0	0	0	0	12	24	35	47	59	70	79	82	80	79	76
0.03	0	0	0	0	0	0	2	14	26	37	49	60	68	72	71	69	66
0.06	0	0	0	0	0	0	0	9	20	32	43	54	62	66	65	63	60
0.12	0	0	0	0	0	0	0	3	14	25	37	47	56	60	59	57	55
0.25	5	1	0	0	0	0	0	1	10	20	30	41	50	53	53	50	48
0.5	17	12	3	0	0	0	0	0	6	16	26	35	44	47	46	44	42
1	29	24	14	10	3	1	0	1	5	13	21	30	38	41	40	38	36
2	41	35	26	20	14	10	6	5	7	10	18	26	33	36	35	33	30
4	53	47	37	32	25	20	16	13	10	12	16	23	28	31	30	28	24
8	65	59	49	43	37	31	26	21	18	16	18	23	25	27	25	23	20
16	76	70	60	54	47	41	35	30	26	23	23	24	26	25	24	20	18
32	84	79	69	62	56	50	44	38	33	28	26	26	28	27	23	21	19
64	88	82	72	66	60	53	47	42	36	31	28	25	27	31	30	28	26
128	88	81	71	65	60	53	47	41	35	30	26	24	25	31	46	49	48
256	85	80	69	64	57	51	45	39	33	28	23	21	22	29	50	90	95
512	83	77	67	61	55	48	42	37	30	25	21	18	19	27	48	96	189

Integrals $n_A=n_B=10;\ l_A=l_B=10;\ R=1$

Algorithm based on ellipsoidal coordinates

Number of accurate decimal figures of integrals computed in quadruple precision

Exps	0.005	0.01	0.03	0.06	0.12	0.25	0.5	1	2	4	8	16	32	64	128	256	512
0.005	29	30	35	40	45	51	57	63	69	75	80	84	87	80	79	73	68
0.01	30	28	31	34	40	45	51	57	63	69	74	78	80	74	73	67	61
0.03	35	31	28	29	32	37	42	48	54	59	65	69	71	64	63	58	52
0.06	40	34	29	29	29	32	37	42	48	53	58	63	65	58	57	52	46
0.12	45	40	32	29	28	29	33	36	42	47	52	56	59	52	51	45	40
0.25	51	45	37	32	30	28	29	32	37	41	46	50	52	46	44	39	33
0.5	57	51	42	37	33	29	28	29	32	36	40	44	46	40	38	32	27
1	63	57	48	42	36	32	29	28	29	32	36	39	40	34	32	27	21
2	69	63	54	48	42	37	32	29	28	29	31	34	35	28	26	22	16
4	75	69	59	53	47	41	36	32	29	29	29	29	30	24	22	16	10
8	80	74	65	58	52	46	40	36	31	29	28	28	27	21	17	11	6
16	84	78	69	63	56	50	44	39	34	29	28	28	25	20	14	9	3
32	87	80	71	65	59	53	46	40	36	30	27	25	26	20	15	10	4
64	80	74	64	58	52	46	40	34	28	24	21	19	20	28	20	17	12
128	79	73	63	57	51	44	38	32	27	22	17	14	15	20	44	39	33
256	73	67	58	52	45	39	32	26	22	16	11	9	9	17	39	88	83
512	68	61	52	46	40	33	27	21	15	10	6	3	4	12	33	83	186

Figure 10: Accurate decimal figures in quadruple precision for overlap integrals with $N_A = N_B = 20$, $L_A = L_B = 10$

From these figures, it is clear that:

- Algorithms 1 and 2 are complementary in the sense that algorithm 1 works better for large scaled exponents whilst algorithm 2 works better for smaller exponents.
- Though the accuracy of algorithm 2 is roughly higher, neither algorithm 1 or 2 in double precision give sufficient accuracy in the whole range of exponents.

Figures 4 and 5 enable the same comparison in case of integrals computed in quadruple precision. It is clear now that

- Algorithm 1 can be confidently used except for very small scaled exponents (lower than 0.15) whilst algorithm 2 gives satisfactory results in the whole range of exponents studied.
- Algorithm 2 downgrades when one of the exponents is very high (~ 500) and the other, moderate (~ 8).

In the second test, the results of both algorithms are compared in a case of higher quantum numbers: $N_A = N_B = 20$, $L_A = L_B = 10$, $-10 \leq M \leq 10$ ($n_A = n_B = 10$ in our notation). Figure 6 shows the order of magnitude of these integrals as a function of the scaled exponents in the same range as before. Now integrals have meaningful values for exponents as large as 60, notably higher than in test 1.
Figs 7 and 8 fully confirm the previous conclusions reached in test 1: algorithms are complementary and double precision is not sufficient. Furthermore, comparing figs 2 and 3 with 7 and 8 it becomes evident the quick downgrading of the results of algorithm 1 in double precision as the L_A and L_B quantum number increase. Figures 9 and 10 show that quadruple precision is not sufficient to reach an acceptable final precision in these integrals. On the contrary, algorithm 2 still works well in almost the whole range of scaled exponents; it only fails when an exponent is very high (~ 500) and the other is moderate (~ 8). Fortunately, these integrals are small (10^{-10} to 10^{-14}) and just in these cases algorithm 1 gives sufficent accuracy.
The algorithms used for computing the $A_j(\beta)$ and $B_j(\nu)$ integrals are fully stable (see appendix A), and so are the computations of the $a_p^{nn'}$ and $\alpha_{kj}^{LM\,L'M}$ constants. The accuracy losses come from the cancellations between the positive and negative terms appearing in the summation of eq(73).

6.4 Shift operators for two-center one-electron integrals: an alternative algorithm

The algorithm described in the previous section 6.2 has proved to be sufficiently accurate for one-electron two-center integrals in a wide range of exponent values for fairly high quantum numbers and it has been adopted for computing this type of integrals. Nevertheless, as some algorithms for Coulomb integrals that will be described below require overlap integrals with rather high quantum numbers, a third algorithm has been developed to compute them in these extreme cases.

In this alternative approach, the master formula for the overlap integral is written as:

$$\langle\, \chi^{n}_{LM} \,|\, \chi^{n'}_{L'M'} \,\rangle = (-1)^{L} \sum_{k=0}^{L_<} \mathscr{P}^{LML'M'}_{k}(\mathbf{R})\; \mathcal{S}^{nL\,n'L'}_{k}(R,\zeta,\zeta') \tag{81}$$

where

$$\begin{aligned} \mathcal{S}^{nL\,n'L'}_{k}(R,\zeta,\zeta') &= \left(-\frac{\partial}{\partial\zeta}\right)^{n} \left(-\frac{\partial}{\partial\zeta'}\right)^{n'} \left(-\frac{1}{\zeta}\,\frac{\partial}{\partial\zeta}\right)^{L} \left(-\frac{1}{\zeta'}\,\frac{\partial}{\partial\zeta'}\right)^{L'} \\ &\times \left(\frac{1}{R}\,\frac{\partial}{\partial R}\right)^{L+L'-k} f(R,\zeta,\zeta') \end{aligned} \tag{82}$$

Derivation of explicit expressions for the $\mathcal{S}^{nL\,n'L'}_{k}$ *coefficients* is simple if the following expression is taken for the basic integral:

$$\langle\, 0s \,|\, 0s' \,\rangle = \sqrt{8\,\pi}\; R \int_0^1 du\; \hat{k}_{-1/2}(\zeta_u\, R) \tag{83}$$

The action of the three Bessel operators on the modified Macdonald functions is straightforward and gives:

$$\begin{aligned} S^{nLn'L'}_{k}(R,\zeta,\zeta') &= (-1)^{L+L'+k}\; \sqrt{8\,\pi}\; R^{2k+1} \left(-\frac{\partial}{\partial\zeta}\right)^{n} \left(-\frac{\partial}{\partial\zeta'}\right)^{n'} \\ &\times \int_0^1 du\; u^{L}\; (1-u)^{L'}\; \hat{k}_{-k-1/2}(\zeta_u\, R) \end{aligned} \tag{84}$$

There are now two possibilities. If the derivative operators are expressed in terms of Bessel operators with the aid of eq(37), after some algebra, it comes:

$$\begin{aligned} \mathcal{S}^{nL\,n'L'}_{k}(R,\zeta,\zeta') &= \frac{(-1)^{L+L'+k}\; \sqrt{8\pi}\; R^{2k+1}}{(2\zeta)^{n}\; (2\zeta')^{n'}} \sum_{\substack{i= \\ E[\frac{(n+1)}{2}]}}^{n} \sum_{\substack{i'= \\ E[\frac{(n'+1)}{2}]}}^{n'} c^{n}_{i}(\zeta R)\; c^{n'}_{i'}(\zeta' R) \\ &\times \int_0^1 du\; u^{L+i}\; (1-u)^{L'+i'}\; \hat{k}_{-k-i-i'-1/2}(\zeta_u R) \end{aligned} \tag{85}$$

where $0 \le k \le \min(L, L')$ and:

$$c^{n}_{i}(\zeta R) = \frac{(-1)^{n+i}\; n!\; (2\,\zeta^2\; R^2)^{i}}{(2i-n)!\; (n-i)!} \tag{86}$$

The pending integral can be computed by numerical methods. Alternatively, the problem can be reduced to compute integrals with the general form:

$$\mathscr{K}^{p,p'}_{-m-1/2}(w,w') = \int_0^1 du\; u^p\; (1-u)^{p'}\; \hat{k}_{-m-1/2}\left(\sqrt{w^2u + w'^2(1-u)}\right) \tag{87}$$

which have been discussed elsewhere [18, 19].

In the second possibility, the integral of eq(84) can be solved and, next, the derivative operators are applied. In order to do this, we carry ut the expansion of the Macdonald function in Gegenbauer polynomials and integate term by term. After some cumbersome algebra, the final result can be written as:

$$S_k^{nLn'L'} = \left(-\frac{\partial}{\partial\zeta}\right)^n\; \left(-\frac{\partial}{\partial\zeta'}\right)^{n'}\; \frac{(-1)^{L+L'+k}\;\sqrt{8\,\pi}\;2^{2k+1}}{(\zeta^2-\zeta'^2)^{k+1/2}}\; \sum_{j=0}^{L+L'-2k}\; \mathscr{L}^{LL'}_{k+1/2}(j)\; M_{k+1/2+j} \tag{88}$$

where

$$\begin{aligned}\mathscr{L}^{LL'}_{k+1/2}(j) &\equiv (-1)^j\;\sqrt{\pi}\;\frac{(k+1/2+j)\;(2k+j)!}{2^{k-1/2}\;j!} \\ &\times \sum_{i=0}^{L'-k}\frac{(-1)^i\;(L'-k)!\;(L-k+i)!\;(L+i)!}{(L'-k-i)!\;(L-k+i-j)!\;(L+k+1+j+i)!\;i!}\end{aligned} \tag{89}$$

and

$$M_{k+1/2+j} \equiv I_{k+1/2+j}\left(\frac{R\;(\zeta-\zeta')}{2}\right)\; K_{k+1/2+j}\left(\frac{R\;(\zeta+\zeta')}{2}\right) \tag{90}$$

Defining $\alpha = \zeta + \zeta'$ and $\alpha' = \zeta - \zeta'$, and taking into account that:

$$\left(-\frac{\partial}{\partial\zeta}\right)^n\; \left(-\frac{\partial}{\partial\zeta'}\right)^{n'} = (-1)^{n+n'}\; \sum_{p=0}^{n+n'} c_p^{nn'}\; \left(\frac{\partial}{\partial\alpha}\right)^{n+n'-p}\; \left(\frac{\partial}{\partial\alpha'}\right)^p \tag{91}$$

with

$$c_p^{nn'} = (-1)^p \sum_{\substack{i=\max(0,\\ p-n')}}^{\min(n,p)} \frac{(-1)^i\;n!\;n'!}{(n-i)!\;(n'-p+i)!\;(p-i)!\;i!} \tag{92}$$

a compact expression is attained:

$$\begin{aligned}S_k^{nLn'L'} &= (-1)^{n+n'+L+L'+k}\;\sqrt{8\,\pi}\;2^{2k+1}\; \sum_{j=0}^{L+L'-2k}\; \mathscr{L}^{LL'}_{k+1/2}(j) \\ &\times \sum_{p=0}^{n+n'} c_p^{nn'}\; F^{(n+n'-p)}_{k+1/2,j}(\alpha_j,R)\; G^{(p)}_{k+1/2,j}(\alpha'_j,R)\end{aligned} \tag{93}$$

where:

$$F^{(m)}_{k+1/2,j}(\alpha,R) = \left(\frac{\partial}{\partial\alpha}\right)^m \frac{K_{k+1/2+j}(\alpha R/2)}{\alpha^{k+1/2}} \tag{94}$$

$$G^{(m)}_{k+1/2,j}(\alpha',R) = \left(\frac{\partial}{\partial\alpha'}\right)^m \frac{I_{k+1/2+j}(\alpha' R/2)}{\alpha'^{k+1/2}} \tag{95}$$

Functions $F^{(m)}_{k+1/2,j}(\alpha,R)$ and $G^{(m)}_{k+1/2,j}(\alpha',R)$ have different expressions depending on the formula taken for the products of powers by Bessel functions. Thus, taking derivatives directly with the aid of Leibnitz rule gives:

$$\begin{aligned} F^{(m)}_{k+1/2,j}(\alpha,R) &= \frac{(-1)^m}{(k-1/2)!\;\alpha^{m+k+1/2}} \sum_{i=0}^{m} \binom{m}{i} (m+k-1/2-i)! \left(\frac{\alpha\,R}{4}\right)^i \\ &\times \sum_{r=0}^{i} \binom{i}{r} K_{k+1/2+j-i+2r}(\alpha R/2) \end{aligned} \tag{96}$$

and

$$\begin{aligned} G^{(m)}_{k+1/2,j}(\alpha',R) &= \frac{(-1)^m}{(k-1/2)!\;\alpha'^{m+k+1/2}} \sum_{i=0}^{m} \binom{m}{i} (m+k-1/2-i)! \left(-\frac{\alpha'\,R}{4}\right)^i \\ &\times \sum_{r=0}^{i} \binom{i}{r} I_{k+1/2+j-i+2r}(\alpha' R/2) \end{aligned} \tag{97}$$

If, as an aternative, we write:

$$F^{(m)}_{k+1/2,j}(\alpha,R) = \left(\frac{R}{2}\right)^{k+1/2} \left(\frac{\partial}{\partial\alpha}\right)^m \left(\frac{\alpha\,R}{2}\right)^j \hat{k}_{-k-1/2-j}(\alpha R/2) \tag{98}$$

and

$$G^{(m)}_{k+1/2,j}(\alpha',R) = \left(\frac{R}{2}\right)^{k+1/2} \left(\frac{\partial}{\partial\alpha'}\right)^m \left(\frac{\alpha'\,R}{2}\right)^j \frac{I_{k+1/2+j}(\alpha' R/2)}{(\alpha'\,R/2)^{k+1/2+j}} \tag{99}$$

Leibnitz rule gives:

$$\begin{aligned} F^{(m)}_{k+1/2,j}(\alpha,R) &= \left(\frac{R}{2}\right)^{k+1/2+j} m!\; j!\; \alpha^{j-m} \sum_{\substack{p=\max(0,\\ m-j)}}^{m} \frac{(-1)^p\;(\alpha\,R/2)^{2p}}{(m-p)!\;(j-m+p)!} \\ &\times \sum_{i=0}^{E\left(\frac{p}{2}\right)} \frac{(-1)^i}{(p-2i)!\;i!\;(\alpha^2\,R^2/2)^i}\; \hat{k}_{-k-1/2-j-p+i}(\alpha R/2) \end{aligned} \tag{100}$$

and

$$G^{(m)}_{k+1/2,j}(\alpha',R) = \left(\frac{R}{2}\right)^{k+1/2+j} m!\; j!\; {\alpha'}^{j-m} \sum_{\substack{p=\max(0,\\ m-j)}}^{m} \frac{(\alpha'\,R/2)^{2p}}{(m-p)!\;(j-m+p)!} \times \sum_{i=0}^{E\left(\frac{p}{2}\right)} \frac{1}{(p-2i)!\;i!\;(\alpha'^2\,R^2/2)^i}\; \frac{I_{k+1/2+j+p-i}(\alpha' R/2)}{(\alpha'\,R/2)^{k+1/2+j+p-i}} \tag{101}$$

Notice that, whereas eqs(96) and (100) are free of cancellation issues, eqs(97) and (99) may be not. Therefore, the former are preferable.

7 Coulomb integrals

The Coulomb integrals between four Slater functions are defined as:

$$[\,\chi^{n_A}_{L_A\,M_A}\;\chi^{n'_A}_{L'_A\,M'_A}\,|\,\chi^{n_B}_{L_B\,M_B}\;\chi^{n'_B}_{L'_B\,M'_B}\,] \equiv \int d\mathbf{r} \int d\mathbf{r}'\; \chi^{n_A}_{L_A\,M_A}(\zeta_A,\mathbf{r}_A)\;\chi^{n'_A}_{L'_A\,M'_A}(\zeta'_A,\mathbf{r}_A) \times\; \chi^{n_B}_{L_B\,M_B}(\zeta_B,\mathbf{r}'_B)\;\chi^{n'_B}_{L'_B\,M'_B}(\zeta'_B,\mathbf{r}'_B)\;\frac{1}{|\mathbf{r}-\mathbf{r}'|} \tag{102}$$

Since one-center STO distributions can be expressed in terms of STO:

$$\chi^{n}_{L\,M}(\zeta_A,\mathbf{r})\;\chi^{n'}_{L'\,M'}(\zeta'_A,\mathbf{r}) = \sum_l \sum_m \alpha^{LM\;L'M'}_{L+L'-2l\;m}\; z^m_{L+L'-2l}(\mathbf{r})\; r^{n+n'+2l-2}\; e^{-(\zeta_A+\zeta'_A)\,r} \tag{103}$$

the integrals of eq (102) are linear combinations of more simple integrals $[\,\chi^{n}_{lm}\,|\,\chi^{n'}_{l'm'}\,]$:

$$[\,\chi^{n_A}_{L_A\,M_A}\;\chi^{n'_A}_{L'_A\,M'_A}\,|\,\chi^{n_B}_{L_B\,M_B}\;\chi^{n'_B}_{L'_B\,M'_B}\,] = \sum_l \sum_m \sum_{l'} \sum_{m'}\; \alpha^{L_AM_A\;L'_AM'_A}_{L_A+L'_A-2l\;m}\;\alpha^{L_BM_B\;L'_BM'_B}_{L_B+L'_B-2l'\;m'}\;[\,\chi^{n}_{lm}\,|\,\chi^{n'}_{l'm'}\,] \tag{104}$$

where $0 \le l \le [(L_A+L'_A)/2]$, $0 \le l' \le [(L_B+L'_B)/2]$, each the sums over m and m' contains two terms at most, and:

$$\begin{aligned}[\,\chi^{n}_{lm}\,|\,\chi^{n'}_{l'm'}\,] &\equiv [\,\chi^{n}_{lm}(\zeta,\mathbf{r}_A)\,|\,\chi^{n'}_{l'm'}(\zeta',\mathbf{r}'_B)\,] \equiv \int d\mathbf{r} \int d\mathbf{r}'\; \chi^{n}_{lm}(\zeta,\mathbf{r}_A)\;\chi^{n'}_{l'm'}(\zeta',\mathbf{r}'_B)\;\frac{1}{|\mathbf{r}-\mathbf{r}'|} \\ &= \int d\mathbf{r} \int d\mathbf{r}'\; z^m_l(\mathbf{r}_A)\; r_A^{n_A-1}\; e^{-\zeta\, r_A}\; z^{m'}_{l'}(\mathbf{r}'_B)\; r'^{n_B-1}_B\; e^{-\zeta'\, r'_B}\;\frac{1}{|\mathbf{r}-\mathbf{r}'|}\end{aligned} \tag{105}$$

where we have used the decomposition of the product of regular harmonics in harmonics, and taken $\zeta = \zeta_A + \zeta'_A$ and $\zeta' = \zeta_B + \zeta'_B$.
Eq 105 can be written in the compact form:

$$
\begin{aligned}
[\, \chi^{n}_{lm} \,|\, \chi^{n'}_{l'm'} \,] &= \delta_{mm'} \int d\mathbf{r}\; V^{n}_{lm}(\mathbf{r})\; \chi^{n'}_{l'm'}(\mathbf{r}_B) \\
&= \int d\mathbf{r}\; V^{n}_{l}(r) \left[z^{m}_{l}(\mathbf{r})\; z^{m}_{l'}(\mathbf{r}_B)\; r_B^{2k} \right] \frac{e^{-\zeta' r_B}}{r_B} \qquad (106)
\end{aligned}
$$

where

$$
\begin{aligned}
V^{n}_{l}(r) = \frac{4\pi}{(2l+1)\;\zeta^{n+1}} \Bigg\{ & \frac{(n+2l+1)!}{(2l)!}\; \frac{\gamma(2l+1,\zeta\, r)}{(\zeta\; r)^{2l+1}} \\
- \;\; & e^{-\zeta\, r}\; (\zeta r)^{i} \sum_{i=0}^{n-1} \left[\frac{(n+2l+1)!}{(i+2l+1)!} - \frac{n!}{i!} \right] \Bigg\} \qquad (107)
\end{aligned}
$$

For odd n', $e^{-\zeta' r_B}/r_B$ must be replaced by $e^{-\zeta' r_B}$.
A first general expression can be by direct substitution of the potential of eq(107) into the definition of eq(106) gives:

$$
\begin{aligned}
[\, \chi^{n}_{LM} \,|\, \chi^{n'}_{L'M'} \,] = \delta_{MM'}\; \frac{4\pi}{(2L+1)} \Bigg\{ & \frac{(n+2L+1)!}{\zeta^{n+2L+2}} \left[\int d\mathbf{r}\; \frac{z^{M}_{L}(\mathbf{r})\; \chi^{n'}_{L'M'}(\mathbf{r}_B)}{r^{2L+1}} \right. \\
- \;\; & \left. \sum_{j=0}^{2L} \frac{\zeta^{j}}{j!} \int d\mathbf{r}\; z^{M}_{L}(\mathbf{r})\; r^{j-2L-1}\; e^{-\zeta r}\; \chi^{n'}_{L'M'}(\mathbf{r}_B) \right] \\
- \;\; & \frac{1}{\zeta^{n+1}} \sum_{i=0}^{n-1} \left[\frac{(n+2L+1)!}{(i+2L+1)!} - \frac{n!}{i!} \right] \zeta^{i} \int d\mathbf{r}\; z^{M}_{L}(\mathbf{r})\; r^{i}\; e^{-\zeta r}\; \chi^{n'}_{L'M'}(\mathbf{r}_B) \Bigg\} \qquad (108)
\end{aligned}
$$

The last term in the r.h.s. is a sum of ordinary overlap integrals which have been previously discussed. The first term can be regarded as an overlap integral with $\zeta = 0$ and negative index n. The second term is a sum of overlap integrals with negative n index that can be attained either by translation methods or by recurrence relations.
This integral can be written also as:

$$
\begin{aligned}
[\, \chi^{n}_{LM} \,|\, \chi^{n'}_{L'M'} \,] = & \frac{(n+2L+1)!}{(2L+1)!\;\zeta^{n}}\; \frac{(n'+2L'+1)!}{(2L'+1)!\;\zeta'^{n'}}\; [\, \chi^{0}_{LM} \,|\, \chi^{0}_{L'M'} \,] \\
- \;\; & \frac{4\;\pi\;(n+2L+1)!}{(2L'+1)\;\zeta'^{n'+1}\;(2L+1)!\;\zeta^{n}} \sum_{i=0}^{n'-1} \left[\frac{(n'+2L'+1)!}{(i+2L'+1)!} - \frac{n'!}{i!} \right] \zeta'^{i}\; \langle\, \chi^{0}_{LM} \,|\, \chi^{i+1}_{L'M'} \,\rangle \\
- \;\; & \frac{4\pi}{(2L+1)\;\zeta^{n+1}} \sum_{i=0}^{n-1} \left[\frac{(n+2L+1)!}{(i+2L+1)!} - \frac{n!}{i!} \right] \zeta^{i}\; \langle\, \chi^{i+1}_{LM} \,|\, \chi^{n'}_{L'M'} \,\rangle \qquad (109)
\end{aligned}
$$

A second general formula for the Coulomb integral of eq(106) is:

$$\begin{aligned}[\chi^n_{LM} \,|\, \chi^{n'}_{L'M'} \,] &= \delta_{MM'}\, 4\,\pi \sum_l \sum_p B^{LMkL'M}_{lp}\; R^{L+L'+2k-l-2p-1/2} \\ &\times \int_0^\infty dr\; V^n_L(r)\; r^{2p+l+3/2}\; M_{l+1/2} \end{aligned} \tag{110}$$

in which a one-dimension integral appears, that can be solved by numerical or analytical methods[18]. As an alternative, the shift operators approach can be used. This procedure provides a lot of different master formulas depending on the expression taken for the basic integral. We will just report here a pair of ilustrative examples.

As it has been commented previously –see sec 3– shift operators allow us to write the general integral as:

$$[\chi^n_{LM} \,|\, \chi^{n'}_{L'M'} \,] = \sum_{k=0}^{L_<} \mathscr{P}^{LML'M'}_k(\mathbf{R})\; J^{nLn'L'}_k \tag{111}$$

where $\mathscr{P}^{LML'M'}_k(\mathbf{R})$ are the functions defined in ec(34) and

$$J^{nLn'L'}_k = \left(-\frac{\partial}{\partial\zeta}\right)^n \left(-\frac{1}{\zeta}\frac{\partial}{\partial\zeta}\right)^L \left(-\frac{\partial}{\partial\zeta'}\right)^{n'} \left(-\frac{1}{\zeta'}\frac{\partial}{\partial\zeta'}\right)^{L'} \left(\frac{1}{R}\frac{\partial}{\partial R}\right)^{L+L'-k} [\chi \,|\, \chi' \,] \tag{112}$$

According to the Fourier transform technique:

$$[\chi \,|\, \chi' \,] \equiv f(R,\zeta,\zeta') \equiv [\chi^0_{00} \,|\, \chi^0_{00} \,] = 16\,\pi\,\sqrt{2\,\pi}\; R^{-1/2} \int_0^\infty dk\; \frac{k^{-1/2}\; J_{1/2}(kR)}{(\zeta^2+k^2)\;(\zeta'^2+k^2)} \tag{113}$$

and writing the derivative operators in terms of Bessel operators the application of the operators is trivial and gives:

$$\begin{aligned} J^{nLn'L'}_k &= \frac{8\pi^2\;\sqrt{2\pi}\;(-1)^{L+L'-k}}{R^{L+L'-k+1/2}} \sum_i \sum_{i'} c^{Ln}_i(\zeta)\; c^{L'n'}_{i'}(\zeta') \\ &\times \int_0^\infty dk\; \frac{k^{L+L'-k-1/2}\; J_{L+L'-k+1/2}(kR)}{(\zeta^2+k^2)^{L+1+i}\;(\zeta'^2+k^2)^{L'+1+i'}} \end{aligned} \tag{114}$$

where $E\left(\frac{n+1}{2}\right) \le i \le n$, $E\left(\frac{n'+1}{2}\right) \le i' \le n'$,and the functions $c^{Ln}_i(\zeta)$ are:

$$c^{ln}_i(\zeta) = \sqrt{\frac{2}{\pi}}\; \frac{2^l\; n!\;(l+i)!\;(2\zeta)^{2i-n}\;(-1)^{n+i}}{(n-i)!\;(2i-n)!} \tag{115}$$

Notice that one-dimension integrals of only one type appear.

The semiinfinite integrals with oscillatory integrands of eq(114) can be replaced by integrals with finite limits and nonoscillatory integrands by means of Feynman transform:

$$\frac{1}{(\zeta^2+k^2)^{p+1}\ (\zeta'^2+k^2)^{p'+1}} = \frac{(p+p'+1)!}{p!\ p'!}\ \int_0^1 du\ \frac{u^p\ (1-u)^{p'}}{(\zeta^2\ u+\zeta'^2\ (1-u)+k^2)^{p+p'+2}} \quad (116)$$

changing the order of the integrals and taking into account that:

$$\begin{aligned}\int_0^\infty dk\ (k\,R)^{l-1/2}\ J_{l+1/2}(kR)\ \frac{1}{(a^2+k^2)^{p+1}} &= \frac{R^{2p+1}}{p!\ 2^p}\ \int_0^1 dt\ t^{2p+1}\ \hat{k}_{l-p-1/2}(aRt)\\ &= \frac{(aR)^{2l}}{p!\ 2^p\ a^{2p+1}}\ \int_0^1 dt\ t^{2l}\ \hat{k}_{p-l+1/2}(aRt) \quad (117)\end{aligned}$$

This leads to:

$$\begin{aligned}J_k^{nL\,n'L'}(R,\zeta,\zeta') = \frac{(-1)^{L+L'+k}\ 8\,\pi\,\sqrt{2\pi}\ R^{2k+3}}{(2\zeta)^n\ (2\zeta')^{n'}}\ &\sum_{\substack{i=\\ E[\frac{(n+1)}{2}]}}^{n}\ \sum_{\substack{i'=\\ E[\frac{(n'+1)}{2}]}}^{n'}\ c_i^n(\zeta R)\ c_{i'}^{n'}(\zeta' R)\\ \times \int_0^1 du\ u^{L+i}\ (1-u)^{L'+i'}\ &\int_0^1 dt\ t^{2(L+L'+i+i'+1)+1}\ \hat{k}_{-k-i-i'-3/2}(\zeta_u Rt) \quad (118)\end{aligned}$$

where:

$$c_i^n(\zeta R) = \frac{(-1)^{n+i}\ n!\ (2\,\zeta^2\ R^2)^i}{(2i-n)!\ (n-i)!} \quad (119)$$

The analytical solution of the innermost integrals follows immediately from

$$\int dx\ x^{2m+1}\ \hat{k}_\nu(\alpha x) = -\frac{m!}{2(\alpha^2/2)^{m+1}}\ \sum_{i=0}^{m}\frac{(\alpha^2\,x^2/2)^i}{i!}\ \hat{k}_{\nu+m+1-i}(\alpha x) \quad (120)$$

and the second integral can be solved with numerical methods.
Eq(118) allows also to separate the long- and short-range contributions. The former is attained by bringing the upper limit of the innermost integral to infinity, and the latter by integrating over $1 \le t \le \infty$. Notice that the long-range contribution must coincide with

$$\begin{aligned}[\,\chi_{lm}^n\,|\,\chi_{l'm'}^{n'}\,]_{R>>} &= 4\,\pi^2\ \frac{(-1)^{l'}\ \sqrt{\pi}\ (l+l'-1/2)!}{(l+1/2)!\ (l'+1/2)!}\ \frac{(n+2l+1)!\ (n'+2l'+1)!}{\zeta^{n+2l+2}\ \zeta'^{n'+2l'+2}}\\ &\times \sum_{m''}^{n}\alpha_{l+l'\ m''}^{lm\,l'm'}\ \frac{z_{l+l'}^{m''}(\mathbf{R})}{R^{2(l+l')+1}} \quad (121)\end{aligned}$$

The solution in case of equal exponents is straightforward by taking $\zeta = \zeta'$ in eq(114) and solving the pending integral with:

$$\int_0^\infty dk\ (k\,R)^{l-1/2}\ \frac{J_{l+1/2}(kR)}{(a^2+k^2)^{p+1}} = \frac{1}{R\,a^{2p+2}}\left[2^{l-1/2}\ (l-1/2)! - \sum_{i=0}^{p}\frac{(a^2\,R^2/2)^i}{i!}\ \hat{k}_{l+1/2-i}(aR)\right]$$

$$= \frac{1}{R\,a^{2p+2}}\ \frac{(p-l-1/2)!}{p!\ 2^{l+1/2}}\ \sum_{i=0}^{p-l}\frac{(l-p)_i\ 2^i}{(2l-2p)_i\ i!}\ \gamma(2l+1+i,aR) \qquad \text{for } p \geq l \tag{122}$$

$$= \frac{1}{R\,a^{2p+2}}\ \frac{(l-p-3/2)!}{p!\ 2^{2p-l+3/2}}\ \sum_{i=0}^{l-p-1}\frac{(p+1-l)_i\ 2^i}{(2p+2-2l)_i\ i!}\ \gamma(2p+2+i,aR) \qquad \text{for } p < l$$

where $p = L + L' + i + i' + 1$, $l = L + L' - k$ and $a = \zeta$.
As a second example, we will consider the generalization of

$$[\,\chi\,|\,\chi'\,] = 16\,\pi^2\left\{\frac{1}{\zeta^2\ \zeta'^2\ R} + \frac{1}{(\zeta^2-\zeta'^2)}\left[\frac{1}{\zeta}\ \int_1^\infty du\ e^{-\zeta R u} - \frac{1}{\zeta'}\ \int_1^\infty du\ e^{-\zeta' R u}\right]\right\} \tag{123}$$

which is interesting because, in this case, the shift operators technique allows to separate the long- and short-range contributions as well as to obtain simple expressions for both.
First, we write:

$$J_k^{nLn'L'} = J_k^{nLn'L'}(long) - J_k^{nLn'L'}(short) \tag{124}$$

where

$$J_k^{nLn'L'}(long) = \left(-\frac{\partial}{\partial\zeta}\right)^n\left(-\frac{1}{\zeta}\frac{\partial}{\partial\zeta}\right)^L\left(-\frac{\partial}{\partial\zeta'}\right)^{n'}\left(-\frac{1}{\zeta'}\frac{\partial}{\partial\zeta'}\right)^{L'}\left(\frac{1}{R}\frac{\partial}{\partial R}\right)^{L+L'-k}\frac{16\,\pi^2}{\zeta^2\ \zeta'^2\ R} \tag{125}$$

Application of shift operators is straightforward since the variables are uncoupled, and gives:

$$J_k^{nLn'L'}(long) = \frac{4\ (-1)^k\ \pi^{5/2}\ (L+L'-k-1/2)!}{2^k\ (L+1/2)!\ (L'+1/2)!}\ \frac{(2L+n+1)!\ (2L'+n'+1)!\ R^{2k}}{\zeta^{2L+n+2}\ \zeta'^{2L'+n'+2}\ R^{2L+2L'+1}} \tag{126}$$

Derivation of the expression for the short-range term is a bit cumbersome. This term is:

$$J_k^{nLn'L'}(short) = \left(-\frac{\partial}{\partial\zeta}\right)^n\left(-\frac{1}{\zeta}\frac{\partial}{\partial\zeta}\right)^L\left(-\frac{\partial}{\partial\zeta'}\right)^{n'}\left(-\frac{1}{\zeta'}\frac{\partial}{\partial\zeta'}\right)^{L'}\left(\frac{1}{R}\frac{\partial}{\partial R}\right)^{L+L'-k}[\,\chi\,|\,\chi'\,]_{short} \tag{127}$$

where

$$[\,\chi\,|\,\chi'\,]_{short} = \sqrt{\frac{2}{\pi}}\ 16\,\pi^2\ \frac{1}{(\zeta^2-\zeta'^2)}\ \int_1^\infty du\ \left[\frac{\hat{k}_{1/2}(\zeta R u)}{\zeta} - \frac{\hat{k}_{1/2}(\zeta' R u)}{\zeta'}\right] \tag{128}$$

Bearing in mind eq(34), we rewrite this term as:

$$J_k^{nLn'L'}(short) = \sum_i \sum_{i'} c_i^n(\zeta)\; c_{i'}^{n'}(\zeta')\; \left(-\frac{1}{\zeta}\frac{\partial}{\partial\zeta}\right)^{L+i}\; \left(-\frac{1}{\zeta'}\frac{\partial}{\partial\zeta'}\right)^{L'+i'} \times \left(\frac{1}{R}\frac{\partial}{\partial R}\right)^{L+L'-k} [\,\chi\,|\,\chi'\,]_{short} \tag{129}$$

where $E\left(\frac{n+1}{2}\right) \le i \le n$, $E\left(\frac{n'+1}{2}\right) \le i' \le n'$ and:

$$c_i^n(\zeta) = \frac{(-1)^{n+i}\; n!\; (2\zeta)^{2i-n}}{(n-i)!\; (2i-n)!\; 2^i} \tag{130}$$

The problem is thus reduced to taking the three pending derivatives. After some algebra, it comes:

$$\begin{aligned} J_k^{nLn'L'}(short) = {} & \sqrt{\frac{2}{\pi}}\; \frac{16\;\pi^2}{\zeta^2-\zeta'^2}\; \frac{(-1)^{n+n'+L+k}\; R^{n+n'+2k+1}}{[(\zeta^2-\zeta'^2)\; R^2/2]^{L+L'}} \\ \times & \sum_{i=E\left(\frac{n+1}{2}\right)}^{n}\; \sum_{i'=E\left(\frac{n'+1}{2}\right)}^{n'} c_i^n(\zeta R)\; c_{i'}^{n'}(\zeta' R)\; \frac{1}{[(\zeta^2-\zeta'^2)\; R^2/2]^{i+i'}} \\ \times & \left\{ \sum_{j=0}^{L+i} \binom{L+i}{j}\; (L+L'+i+i'-j)!\; [(\zeta^2-\zeta'^2)\; R^2/2]^j \right. \\ \times & \int_1^\infty du\; u^{2j+1}\; \hat{k}_{L+L'-k-j-1/2}(\zeta R u) \\ - & \sum_{j'=0}^{L'+i'} \binom{L'+i'}{j'}\; (L+L'+i+i'-j')!\; [-(\zeta^2-\zeta'^2)\; R^2/2]^{j'} \\ \times & \left. \int_1^\infty du\; u^{2j'+1}\; \hat{k}_{L+L'-k-j'-1/2}(\zeta' R u) \right\} \end{aligned} \tag{131}$$

where the pending integrals are:

$$\int_1^\infty du\; u^{2j+1}\; \hat{k}_\nu(zu) = \frac{j!\; 2^j}{(z^2)^{j+1}}\; \sum_{i=0}^{j} \frac{(z^2/2)^i}{i!}\; \hat{k}_{\nu+j+1-i}(z) \tag{132}$$

7.1 Tests on the accuracy of algorithms for Coulomb integrals

The formal developments of the previous sections can be combined in many ways, leading to a huge amount of possible algorithms for the calculation integrals. The analysis of every alternative implies its implementation in a program code and a thorough testing of the results. As a consequence, a previous selection of the possible candidates is mandatory.

For the moment, we have implemented and tested only three algorithms among the more simple ones. In all of them, the final Coulomb integrals are obtained as linear combinations of integrals

$[\ \chi^n_{LM}\,|\,\chi^{n'}_{L'M'}\ ]$, as indicated in eq(104). The algorithms differ in the way the $[\ \chi^n_{LM}\,|\,\chi^{n'}_{L'M'}\ ]$ integrals are computed.

First, a code in double precision based on eq(112) combined with the shift operators technique was attempted (file `coulomb_2010_shiftop_D.f90`). This was an appealing approach because the general Coulomb integrals were reduced to linear combinations of overlap integrals plus one Coulomb integral involving functions with $n \equiv N - L = 0$. Since the quantum numbers appearing in the overlap integrals are twice the values of these numbers in the basis functions, we had to develop a new algorithm for overlap integrals more robust than any other proposed before. Unfortunately, after the new algorithm for overlap integrals was developed and coded, and once the accuracy in the overlap was guaranteed, we found that, for high quantum numbers, big numerical cancellations occur between the first summand in eq(112) and the remaining ones. Because of it, we preferred to try a different solution.

In the second attempt, a code based on the numerical integration of eq(110) was prepared (file `coulomb_2010_intnum_D.f90`). In principle, the algorithm seems to be more robust than the previous one, but there is a problem with the dependence of the integrand with the values of the exponents and the quantum numbers. This dependence is rather involved and makes it difficult to design a good choice of the quadrature points, which is critical in the final result.

In view of this, we have tried a third solution, which is closely related with that already implemented in SMILES, based on eq(108). The algorithm follows closely the presciption of ref[26], but the calculation of the auxiliary functions has been completely redesigned. In this way, we have been able to extend the accuracy of the calculations. We have thus prepared three codes corresponding to double and quadruple precision and multiprecision[27]. The latter has been taken as a reliable reference for all the remaining codes.

Figs 11 to 14 illustrate the quality of the results attained with the double and quadruple versions of the third code (with the multiprecision values taken as a reference). As it can be seen in figs 11 and 12, for high quantum numbers, there is a rather broad range of exponents, defined by the value of the lowest (ζ, ζ') between 4 and 64, in which there is a significant loss of accuracy. Using quadruple precision in this range is sufficient to overcome the problem, as figs 11 and 12 show.

The employment of quadruple precision implies a penalty in computational time by a factor between 10 and 100 with respect to double precision. Since the algorithm is quite fast, the computational cost in quadruple still remains acceptable. Nevertheless, it is always possible to combine both double and quadruple precision in the same code, restricting the use of the quadruple precision to those cases in which a significant loss of accuracy has been detected.

Finally, it should be noticed that the formal developments above reported open the door to many other possible algorithms. However, at this moment, we consider that the current algorithm based on translation, with quadruple precision in the prescripted cases, is sufficiently

satisfactory to fulfill the current requirements in molecular calculations with STO.

Absolute error NA=NA'=6 LA=LA'=5 NB=NB'=6 LB = LB' = 5																	
Double precision																	
Exp+Exp'	0.005	0.01	0.03	0.06	0.12	0.25	0.5	1	2	4	8	16	32	64	128	256	512
0.005	15	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
0.01	18	15	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
0.03	18	18	14	-	-	-	-	-	-	-	-	-	-	-	-	-	-
0.06	18	18	17	14	-	-	-	-	-	-	-	-	-	-	-	-	-
0.12	18	18	17	17	14	-	-	-	-	-	-	-	-	-	-	-	-
0.25	18	18	17	17	16	14	-	-	-	-	-	-	-	-	-	-	-
0.5	18	18	17	17	16	16	13	-	-	-	-	-	-	-	-	-	-
1	18	18	17	17	16	16	16	13	-	-	-	-	-	-	-	-	-
2	18	18	17	17	16	16	16	15	11	-	-	-	-	-	-	-	-
4	18	18	17	17	16	16	16	16	15	10	-	-	-	-	-	-	-
8	18	18	17	17	16	16	16	16	15	13	9	-	-	-	-	-	-
16	18	18	17	17	16	16	16	16	15	14	11	8	-	-	-	-	-
32	18	18	17	17	16	16	16	16	15	14	11	8	4	-	-	-	-
64	18	18	17	17	16	16	16	16	15	14	11	8	4	9	-	-	-
128	18	18	17	17	16	16	16	16	15	14	11	8	4	13	14	-	-
256	18	18	17	17	16	16	16	16	15	14	11	8	4	14	14	14	-
512	18	18	17	17	16	16	16	16	15	14	11	8	4	14	14	14	14

Figure 11: Accurate decimal figures in double precision for Coulomb integrals with $N_A = N_B = N_C = N_D = 6$, $L_A = L_B = L_C = L_D = 5$

Relative error NA=NA'=6 LA=LA'=5 NB=NB'=6 LB = LB' = 5																	
Double precision																	
Exp+Exp'	0.005	0.01	0.03	0.06	0.12	0.25	0.5	1	2	4	8	16	32	64	128	256	512
0.005	8																
0.01	10	8															
0.03	14	13	9														
0.06	14	14	11	8													
0.12	14	14	13	11	8												
0.25	14	14	14	13	11	8											
0.5	14	14	14	14	14	11	8										
1	14	14	14	14	14	14	11	9									
2	14	14	14	14	14	14	13	12	9								
4	14	14	14	14	14	14	14	13	11	7							
8	14	14	14	14	14	14	14	14	12	10	7						
16	14	14	14	14	14	14	14	14	14	12	9	6					
32	14	14	14	14	14	14	14	14	14	12	10	7	2				
64	14	14	14	14	14	14	14	14	13	13	10	6	1	3			
128	14	14	14	14	14	14	14	14	14	12	9	7	3	7	14		
256	14	14	14	14	14	14	14	14	14	13	9	7	3	8	14	14	
512	14	14	14	14	14	14	14	14	14	13	8	7	3	9	14	14	14

Figure 12: Accurate significant figures in double precision for Coulomb integrals with $N_A = N_B = N_C = N_D = 6$, $L_A = L_B = L_C = L_D = 5$

Absolute error NA=NA'=6 LA=LA'=5 NB=NB'=6 LB = LB' = 5																	
Quadruple precision																	
Exp+Exp'	0.005	0.01	0.03	0.06	0.12	0.25	0.5	1	2	4	8	16	32	64	128	256	512
0.005	33																
0.01	36	33															
0.03	37	36	32														
0.06	37	37	36	32													
0.12	37	37	36	36	32												
0.25	37	37	36	36	35	31											
0.5	36	36	36	36	35	35	31										
1	37	36	36	36	35	35	34	30									
2	37	36	36	36	35	35	35	33	29								
4	37	36	37	36	35	35	35	34	32	28							
8	36	36	36	36	35	35	35	34	34	31	27						
16	36	36	36	35	35	35	35	34	34	32	29	25					
32	36	36	36	36	35	35	35	34	34	32	29	25	22				
64	36	36	36	35	35	35	35	34	34	32	29	25	22	18			
128	37	36	36	36	35	35	35	34	34	32	29	25	22	18	30		
256	36	36	36	35	35	35	35	34	34	32	29	25	22	18	33	34	
512	36	36	36	36	35	35	35	34	34	32	29	25	22	18	33	34	33

Figure 13: Accurate decimal figures in quadruple precision for Coulomb integrals with $N_A = N_B = N_C = N_D = 6$, $L_A = L_B = L_C = L_D = 5$

Relative error NA=NA'=6 LA=LA'=5 NB=NB'=6 LB = LB' = 5																	
Quadruple precision																	
Exp+Exp'	0.005	0.01	0.03	0.06	0.12	0.25	0.5	1	2	4	8	16	32	64	128	256	512
0.005	26																
0.01	28	26															
0.03	33	32	26														
0.06	33	32	29	27													
0.12	33	33	31	29	26												
0.25	33	32	33	31	29	26											
0.5	33	33	34	33	31	29	25										
1	33	33	34	32	33	31	29	27									
2	33	33	34	33	33	33	31	30	27								
4	33	32	34	32	33	33	33	31	28	25							
8	33	32	33	33	33	33	33	31	31	29	25						
16	33	33	34	33	33	33	33	33	32	30	27	24					
32	33	33	34	32	33	33	33	33	32	31	29	25	20				
64	33	33	33	33	33	33	33	33	31	31	29	24	19	14			
128	33	32	34	32	33	33	33	33	33	31	28	25	20	15	23		
256	33	32	34	33	33	33	33	33	33	31	28	25	21	15	29	27	
512	33	33	33	33	33	33	33	33	33	31	26	25	21	15	31	28	33

Figure 14: Accurate significant figures in quadruple precision for Coulomb integrals with $N_A = N_B = N_C = N_D = 6$, $L_A = L_B = L_C = L_D = 5$

8 Hybrid integrals

Hybrid integrals of STOs are defined as:

$$[\,\chi^{n_A}_{L_A M_A}\;\chi^{n_B}_{L_B M_B}\,|\,\chi^{n'_A}_{L'_A M'_A}\;\chi^{n''_A}_{L''_A M''_A}\,] \equiv \int d\mathbf{r} \int d\mathbf{r}'\;\chi^{n_A}_{L_A M_A}(\zeta_A, \mathbf{r}_A)\;\chi^{n_B}_{L_B M_B}(\zeta_B, \mathbf{r}_B) \times\;\chi^{n'_A}_{L'_A M'_A}(\zeta'_A, \mathbf{r}'_A)\;\chi^{n''_A}_{L''_A M''_A}(\zeta''_A, \mathbf{r}'_A)\;\frac{1}{|\mathbf{r}-\mathbf{r}'|} \tag{133}$$

To compute the hybrid integrals, the one-center distribution, $\chi^{n'_A}_{L'_A\,M'_A}(\zeta'_A,\mathbf{r}_A)\;\chi^{n''_A}_{L''_A\,M''_A}(\zeta''_A,\mathbf{r}_A)$ is decomposed as a linear combination of one-center distributions –see eq(103). In this way, the general hybrid integral of eq(133) can be expressed as a linear combination of integrals like:

$$[\,\chi^{n_A}_{L_A\,M_A}\;\chi^{n_B}_{L_B\,M_B}\,|\,\chi^{\nu}_{\lambda\,\mu}\,] = \int d\mathbf{r}\int d\mathbf{r}'\chi^{n_A}_{L_A\,M_A}(\zeta_A,\mathbf{r})\;\chi^{n_B}_{L_B\,M_B}(\zeta_B,\mathbf{r}_B)\;\frac{1}{|\mathbf{r}-\mathbf{r}'|}\;\chi^{\nu}_{\lambda\,\mu}(\zeta,\mathbf{r}') \tag{134}$$

where center A has been taken as the coordinates origin and $\zeta \equiv \zeta'_A+\zeta''_A$. The coefficients of the linear combination are those of the decomposition of products of regular spherical harmonics into spherical harmonics.

The problem is thus reduced to the efficient computation of integrals like (134). In the current approach, these integrals are computed starting from some basic integrals which can be chosen as:

$$I^{\nu\lambda\mu}_{nLM} \equiv \int d\mathbf{r}\int d\mathbf{r}'\chi^{n_A}_{L_A\,M_A}(\zeta_A,\mathbf{r}_A)\;\chi^{0}_{00}(\zeta_B,\mathbf{r}_B)\;\frac{1}{|\mathbf{r}-\mathbf{r}'|}\;\chi^{\nu}_{\lambda\,\mu}(\zeta,\mathbf{r}') \tag{135}$$

for integrals with N_B even, and

$$J^{\nu\lambda\mu}_{nLM} \equiv \int d\mathbf{r}\int d\mathbf{r}'\chi^{n}_{L\,M}(\zeta_A,\mathbf{r}_A)\;\chi^{1}_{00}(\zeta_B,\mathbf{r}_B)\;\frac{1}{|\mathbf{r}-\mathbf{r}'|}\;\chi^{\nu}_{\lambda\,\mu}(\zeta,\mathbf{r}') \tag{136}$$

for N_B odd, and translating the factor $|\mathbf{r}-\mathbf{R}_{AB}|^{2E(n_B/2)}\;z^{M_B}_{L_B}(\mathbf{r}-\mathbf{R}_B)$ to center A. In a lined-up axis system –with the Z and Z' axes coincident and the (X,Y) axes parallel to (X',Y')– this translation is very simple and all the integrals with $M \neq \mu$ vanish after integration on ϕ.

We start by translating the factor $|\mathbf{r}-\mathbf{R}_{AB}|^{2E(n_B/2)}$ by:

$$|\mathbf{r}-\mathbf{R}_{AB}|^{2E(n_B/2)} = (r^2+R^2_{AB}-2\,r\,R_{AB}\,\cos\theta)^{E(n_B/2)} \tag{137}$$

where $E(\nu)$ stands for the integer part of ν. This equation yields the recurrence relation:

$$\begin{aligned}
[\,n,L,M;\nu_B+2,0,0\,|\,\nu,\lambda,M\,] = {} & R^2_{AB}\,[\,n,L,M;\nu_B,0,0\,|\,\nu,\lambda,M\,] \\
+ {} & [\,n+2,L,M;\nu_B,0,0\,|\,\nu,\lambda,M\,] \\
- {} & \frac{2\,R_{AB}}{2L+1}\Big\{(L-M+1)\,[\,n,L+1,M;\nu_B,0,0\,|\,\nu,\lambda,M\,] \\
+ {} & (L+M)\,[\,n+2,L-1,M;\nu_B,0,0\,|\,\nu,\lambda,M\,]\Big\}
\end{aligned} \tag{138}$$

that can be used to reach the integrals for $\nu_B = n_B$. In order to get the pertaining values of L_B and M_B, we apply the translation of the solid regular harmonic $z^{M_B}_{L_B}(\mathbf{r}-\mathbf{R}_B)$ to the integrals $[\,n,L,M;n_B,0,0\,|\,\nu,\lambda,M\,]$, by means of

$$z_{L_B}^{M_B}(\mathbf{r}-\mathbf{R}_{AB}) = \sum_{k=|M_B|}^{L_B} \binom{L_B+|M_B|}{k+|M_B|} (-R_{AB})^{L_B-k}\ z_k^{M_B}(\mathbf{r}) \tag{139}$$

followed by the decomposition of the product $z_{L_A}^{M_A}(\mathbf{r})\ z_k^{M_B}(\mathbf{r})$ with

$$z_L^M(\mathbf{r})\ z_{L'}^{M'}(\mathbf{r}) = \sum_l \sum_\mu \alpha_{L+L'-2l\,\mu}^{LM\,L'M'}\ r^{2l}\ z_{L+L'-2l}^{\mu}(\mathbf{r}) \tag{140}$$

where $|\mu| \leq l \leq E[(L+L')/2]$ and, in the lined-up system, the sum over μ contains two terms at most.
This gives:

$$\begin{aligned}[\,n,L,M;n_B,L_B,M_B\,|\,\nu,\lambda,\mu\,] = &\sum_{k=|M_B|}^{L_B} \binom{L_B+|M_B|}{k+|M_B|} (-R_{AB})^{L_B-k} \\ \times &\sum_l \alpha_{L_A+k-2l\,\mu}^{L_A M_A\,kM_B}[\,n+2l,L_A+k-2l,\mu;n_B,0,0\,|\,\nu,\lambda,\mu\,]\end{aligned} \tag{141}$$

8.1 Calculation of the basic hybrid integrals

The basic integrals can be written as:

$$I_{nLM}^{\nu\lambda\mu} = \int d\mathbf{r}\chi_{L_A\,M_A}^{n_A}(\zeta_A,\mathbf{r}_A)\ \chi_{00}^0(\zeta_B,\mathbf{r}_B)\ V_{\lambda\mu}^{\nu}(\zeta,\mathbf{r}) \tag{142}$$

and

$$J_{nLM}^{\nu\lambda\mu} = \int d\mathbf{r}\chi_{L_A\,M_A}^{n_A}(\zeta_A,\mathbf{r}_A)\ \chi_{00}^1(\zeta_B,\mathbf{r}_B)\ V_{\lambda\mu}^{\nu}(\zeta,\mathbf{r}) \tag{143}$$

where $V_{\lambda\mu}^{\nu}(\zeta,\mathbf{r})$ is the potential generated by the one-electron distribution $\chi_{\lambda\,\mu}^{\nu}(\zeta,\mathbf{r}')$. This potential is well known and can be written as:

$$\begin{aligned}V_{\lambda\mu}^{\nu}(\zeta,\mathbf{r}) &= \frac{4\,\pi}{2\lambda+1}\ z_\lambda^\mu(\mathbf{r})\Bigg\{\frac{(\nu+2\lambda+1)!}{\zeta^{\nu+2\lambda+2}\ r^{2\lambda+1}}\left[1-e^{-\zeta r}\ \sum_{j=0}^{2\lambda}\frac{(\zeta\,r)^j}{j!}\right] \\ &+ \frac{e^{-\zeta r}}{\zeta^{\nu+1}}\ \sum_{j=0}^{\nu-1}(\zeta\,r)^j\ \left[\frac{\nu!}{j!}-\frac{(\nu+2\lambda+1)!}{(2\lambda+j+1)!}\right]\Bigg\}\end{aligned} \tag{144}$$

Replacing 144 in 142 this latter can be written as:

$$I_{nLM}^{\nu\lambda\mu} = \sum_l \alpha_{L+\lambda-2l\,0}^{LM\,\lambda\mu}\ A_{lL\lambda}^{n\nu} \tag{145}$$

where:

$$
\begin{aligned}
A^{n\nu}_{lL\lambda} &= \frac{2l+1}{(2\lambda+1)\,\zeta}\left\{\frac{(\nu+2\lambda+1)!}{\zeta^{\nu+2\lambda+1}}\,h_l^{n+L-\lambda-l-1}(\zeta_A,\zeta_B)\right. \\
&- \left.\sum_{j=0}^{2\lambda}\frac{\zeta^j}{j!}\,h_l^{n+L+j-\lambda-l-1}(\zeta_A+\zeta,\zeta_B)\right] + \sum_{j=0}^{\nu-1} h_l^{n+L+j+\lambda-l}(\zeta_A+\zeta,\zeta_B) \\
&\times \left.\left[\frac{\nu!}{j!} - \frac{(\nu+2\lambda+1)!}{(j+2\lambda+1)!}\right]\right\} \qquad (146)
\end{aligned}
$$

$h_l^n(\alpha,\beta)$ being the two-center overlap integrals:

$$
h_l^n(\alpha,\beta) = \int d\mathbf{r}\; r^{n-1}\; z_l^0(\mathbf{r})\; e^{-\alpha r}\;\frac{e^{-\beta r_B}}{r_B} \qquad (147)
$$

For the $J^{\nu\lambda\mu}_{nLM}$ integrals, an equation like (145) also holds replacing h_l^n by H_l^n in eq(147), with:

$$
H_l^n(\alpha,\beta) = \int d\mathbf{r}\; r^{n-1}\; z_l^0(\mathbf{r})\; e^{-\alpha r}\; e^{-\beta r_B} \qquad (148)
$$

The problem is thus reduced to the evaluation of the overlap integrals $h_l^n(\alpha,\beta)$ and $H_l^n(\alpha,\beta)$, which can be accomplished with any of the procedures previously described for overlap integrals. In particular, the current codes compute these integrals by means of the STO translation formulas:

$$
h_l^n(\alpha,\beta) = \frac{4\,\pi\,R_{AB}^{n+l+1}\; e^{-(\alpha+\beta)}}{2l+1}\left[\Phi_l(\beta)\; i_{ln}(\alpha,\beta) + \frac{\phi_l(\beta)\; k_{ln}(\alpha,\beta)}{(\alpha+\beta)^{n+1}}\right] \qquad (149)
$$

$$
\begin{aligned}
H_l^n(\alpha,\beta) &= 4\,\pi\,R_{AB}^{n+l+2}\; e^{-(\alpha+\beta)}\left\{\frac{\beta}{2l+1}\left[\frac{\Phi_{l-1}(\beta)\; i_{ln}(\alpha,\beta)}{2l-1} - \frac{\Phi_l(\beta)\; i_{l+1\,n}(\alpha,\beta)}{2l+3}\right]\right. \\
&+ \left.\frac{1}{\beta\;(\alpha+\beta)^{n+1}}\left[\phi_l(\beta)\; k_{l+1n}(\alpha,\beta) - \phi_{l-1}(\beta)\; k_{ln}(\alpha,\beta)\right]\right\} \qquad l>0 \qquad (150)
\end{aligned}
$$

$$
\begin{aligned}
H_0^n(\alpha,\beta) &= 4\,\pi\,R_{AB}^{n+2}\; e^{-(\alpha+\beta)}\left\{i_{0n}(\alpha,\beta) - \frac{\beta}{3}\; i_{1\,n}(\alpha,\beta)\right. \\
&+ \left.\frac{1}{\beta\;(\alpha+\beta)^{n+1}}\left[\phi_0(\beta)\; k_{1n}(\alpha,\beta) - \left(\phi_0(\beta) + \frac{y^2}{3}\;\phi_1(\beta)\right)\; k_{0n}(\alpha,\beta)\right]\right\} \qquad (151)
\end{aligned}
$$

$$
H_l^n(\alpha,\beta) = \frac{y}{2l+1}\left[h_{l-1}^{n+2}(\alpha,\beta) - h_{l+1}^n(\alpha,\beta)\right] \qquad (152)
$$

with

$$
\begin{aligned}
\Phi_l(\beta) &= \frac{(2\beta)^{l+1/2}\; l!}{\pi^{1/2}\;(2l)!}\; e^{\beta}\; K_{l+1/2}(\beta) \\
&= {}_1F_1(-l;-2l;2\beta) \qquad (153)
\end{aligned}
$$

$$\begin{aligned}\phi_l(\beta) &= (2/\beta)^{l+1/2}\ (l+1/2)!\ I_{l+1/2}(\beta) \\ &= {}_0F_1(l+3/2;\beta^2/4)\end{aligned} \tag{154}$$

$$\begin{aligned}i_{ln}(\alpha,\beta) &= (2/\beta^2)^{l+1/2}\ (l+1/2)!\ e^{\alpha}\ \int_0^1 dt\ t^n\ e^{-\alpha t}\ (\beta t)^{l+1/2}\ I_{l+1/2}(\beta t) \\ &= \sum_{j=0}^{\infty} \frac{(\beta^2/4)^j\ {}_1F_1(1;n+2l+2j+3;\alpha)}{j!\ (l+3/2)_j\ (n+2l+2j+2)}\end{aligned} \tag{155}$$

$$\begin{aligned}k_{ln}(\alpha,\beta) &= e^{\alpha+\beta}\ \frac{(\alpha+\beta)^{n+1}\ l!\ 2^{l+1/2}}{(2l)!\ \pi^{1/2}}\ \int_1^{\infty} dt\ t^n\ e^{-\alpha t}\ (\beta t)^{l+1/2}\ K_{l+1/2}(\beta t) \\ &= \sum_{j=0}^{l} \left(\frac{2\beta}{\alpha+\beta}\right)^j\ e_{n+j}(\alpha+\beta)\ \frac{(-l)_j\ (n+j)!}{j!\ (-2l)_j}\end{aligned} \tag{156}$$

In these equations, $(a)_j$ denotes the corresponding Pochhammer symbol, $K_\nu(z)$ are the Macdonald functions, $I_\nu(z)$ the corresponding Bessel functions, and $e_n(z)$ stands for the truncated exponential:

$$e_n(z) = \sum_{j=0}^{n} \frac{x^j}{j!} \tag{157}$$

The set of Φ_l functions is computed by recursion in a fully stable way:

$$\Phi_{l+1}(\beta) = \Phi_l(\beta) + \frac{\beta^2}{(2l-1)\ (2l+1)}\ \Phi_{l-1}(\beta) \tag{158}$$

starting from $\Phi_0(\beta) = 1$ and $\Phi_1(\beta) = 1 + \beta$.
The set of ϕ_l functions can be computed also by recursion by means of:

$$\phi_{l-1}(\beta) = \phi_l(\beta) + \frac{\beta^2}{(2l+1)\ (2l+3)}\ \phi_{l+1}(\beta) \tag{159}$$

since the relation is stable for backwards recursion, it must be started from $\phi_{l_{max}}(\beta)$ and $\phi_{l_{max}-1}(\beta)$, which are computed by means of eq(154). To improve performance, Miller's algorithm[28] is used.
For the calculation of the $k_{ln}(\alpha,\beta)$, the first row is computed by:

$$k_{0n}(\alpha,\beta) = n!\ e_n(\alpha+\beta) \tag{160}$$

the second row, by:

$$k_{1n}(\alpha,\beta) = k_{0n}(\alpha,\beta) + \frac{\beta}{\alpha+\beta}\; k_{0n+1}(\alpha,\beta) \tag{161}$$

and the remaining ones, by:

$$k_{l+1n}(\alpha,\beta) = k_{ln}(\alpha,\beta) + \frac{\beta^2}{(\alpha+\beta)^2\;(2l+1)\;(2l-1)}\; k_{l-1n+2}(\alpha,\beta) \tag{162}$$

Finally, in the calculation of the $i_{ln}(\alpha,\beta)$, three cases are distinguished:

Case 1: $\beta \leq 1$

The elements $i_{l_{max}\,n}(\alpha,\beta)$ with $n \leq -1$ are computed by means of the second expression in eq(155). Although the sum is infinite, it converges very quickly for these values of β. The remaining elements are computed by means of:

$$i_{ln}(\alpha,\beta) = \frac{1}{2l+3}\;\left[\phi_{l+1}(\beta) + \alpha\; i_{l+1\,n-1}(\alpha,\beta) - (n-1)\; i_{l+1\,n-2}(\alpha,\beta)\right] \tag{163}$$

$$\begin{aligned} i_{l\,n+1}(\alpha,\beta) &= \frac{1}{(2l+3)\;(n+2l+3)}\;\left[(\alpha^2-\beta^2)\; i_{l+1\,n+1}(\alpha,\beta) - (n+1)\;\alpha\; i_{l+1\,n}(\alpha,\beta)\right. \\ &+ \left.(\alpha+2l+3)\;\phi_{l+1}(\beta) + \frac{\beta^2}{2l+5}\;\phi_{l+2}(\beta)\right] \end{aligned} \tag{164}$$

$$\begin{aligned} i_{l\,n}(\alpha,\beta) &= \frac{1}{(2l+3)\;(n+2l+3)\;(n+2l+2)}\;\left\{(\alpha^2-\beta^2)\;\alpha\; i_{l+1\,n+1}(\alpha,\beta)\right. \\ &- \left[(n+1)\;\alpha^2 + (n+2l+3)\;\beta^2\right]\; i_{l+1\,n}(\alpha,\beta) + \alpha^2\;\phi_{l+1}(\beta) \\ &+ \left.(2l+3)\;(\alpha+n+2l+3)\;\phi_l(\beta)\right\} \end{aligned} \tag{165}$$

Case 2: $\beta \geq \alpha + 8$

The elements $i_{l\,-2l_{max}}(\alpha,\beta)$ and $i_{l\,-2l_{max}+1}(\alpha,\beta)$ are computed by eq(155). The remaining elements with $l = l_{max}$ are computed by:

$$\begin{aligned} i_{l\,n+2}(\alpha,\beta) &= \frac{1}{\alpha^2-\beta^2}\;\left[-(n+1)\;(n+2l+2)\; i_{l\,n}(\alpha,\beta)\right. \\ &+ \left.2\,\alpha\;(n+2l+2)\; i_{l\,n+1}(\alpha,\beta) + (n+1-\alpha)\;\phi_l(\beta) - \frac{\beta^2}{2l+3}\;\phi_{l+1}(\beta)\right] \end{aligned} \tag{166}$$

Case 3: $1 < \beta < \alpha + 8$

The elements $i_{l\,n}(\alpha,\beta)$ with $n = n_{min}$ and $l = n_{max} - n_{min}$, and $l = n_{max} - n_{min} - 1$ are computed by eq(155). The elements with $n = n_{min} + 1$ and $l = n_{max} - n_{min} - 1$, and $l = n_{max} - n_{min} - 2$ are computed by:

$$i_{l\,n+1}(\alpha,\beta) = \frac{1}{\alpha}\;\left[(n+2l+2)\; i_{l\,n}(\alpha,\beta) + \frac{\beta^2}{2l+3}\; i_{l+1\,n}(\alpha,\beta) - \phi_l(\beta)\right] \tag{167}$$

and (164) respectively.
The remaining elements with $n = n_{min}$ and $n = n_{min} + 1$ are computed by:

$$i_{l\,n}(\alpha,\beta) = \frac{1}{(n+2l+2)\,(n+2l+3)} \left\{ -\left[\frac{(n+2l+7/2)\,\beta^2}{l+3/2} - \alpha^2 \right] i_{l+1\,n}(\alpha,\beta) \right.$$
$$\left. + \quad \frac{(\alpha^2-\beta^2)\,\beta^2}{(2l+3)\,(2l+5)}\, i_{l+2\,n}(\alpha,\beta) + (\alpha+n+2l+3)\,\phi_l(\beta) + \frac{\beta^2}{2l+3}\,\phi_{l+1}(\beta) \right\} \quad (168)$$

and the remaining elements, by:

$$i_{l-1\,n+2}(\alpha,\beta) = i_{l\,n}(\alpha,\beta) + \frac{\beta^2}{(2l+3)\,(2l+1)}\, i_{l+1\,n}(\alpha,\beta) \quad (169)$$

Finally, the hypergeometrics ${}_1F_1(1;n;\alpha) \equiv F_n(\alpha)$ appearing in eq(155) are computed by backwards recursion:

$$F_n(\alpha) = 1 + \frac{\alpha}{n}\, F_{n+1}(\alpha) \quad (170)$$

starting with the explicit definition

$$F_n(\alpha) = \sum_{j=0}^{\infty} \frac{\alpha^j}{j!} \quad (171)$$

for an index n such that the series converges quickly.

8.2 Tests on the accuracy of algorithms for hybrid integrals

The above exposed algorithms for hybrid integrals have been implemented in FORTRAN at three different levels of accuracy: double precision, quadruple precision and multiprecision[27]. The multiprecision version (with a working precision of 65 decimal digits) has been used as a reference for testing the accuracy of the other two.
Figs 15 to 20 illustrate the accuracy attained in the hybrid integrals with the current algorithm for $N = 6$ and $L = 5$ for the four functions. As it can be seen, there is a wide range of values of the exponents for which the accuracy loss in double precision is dramatic, and the algorithm seems not no be suitable in DP. When quadruple precision is used, the range becomes narrower but it still remains a range –corresponding to values of the exponents that do not appear in usual basis sets– for which all the figures are lost even in quadruple precision. The consequence is rather obvious, if exponents within this range will be used, algorithms based on a different formalism must be investigated. For the moment, the only available solution is based in the Gaussian expansions of the STO, which can be used to cover these pathological cases.

Hybrid integrals: exA=exB; exA'=exB'																	
Accurate decimal places NA=NA'=6 LA=LA'=5 NB=NB'=6 LB = LB' = 5																	
Double precision																	
exA'=exA" exA =exB	0.0025	0.005	0.01	0.03	0.06	0.12	0.25	0.5	1	2	4	8	16	32	64	128	256
0.005	12	16	17	17	17	17	17	17	17	17	17	17	17	17	17	17	17
0.01	9	14	17	17	17	17	17	17	17	17	17	17	17	17	17	17	17
0.03	3	6	12	14	17	17	17	17	17	17	17	17	17	17	17	17	17
0.06	0	3	8	11	14	16	16	16	16	16	17	17	17	17	17	17	17
0.12	0	2	5	7	11	13	16	16	16	16	16	16	16	16	16	16	16
0.25	0	0	1	5	8	11	14	16	16	16	16	16	16	16	16	16	16
0.5	0	0	0	1	4	7	10	14	16	16	16	16	16	16	16	16	16
1	0	0	0	0	0	3	7	10	13	15	15	15	15	15	15	15	15
2	0	0	0	0	0	0	3	6	9	13	15	15	15	15	15	15	15
4	0	0	0	0	0	0	0	3	6	9	12	14	14	14	15	14	14
8	0	0	0	0	0	0	0	1	3	7	10	12	12	13	12	13	12
16	0	0	0	0	0	0	0	0	3	5	8	11	12	12	12	12	12
32	0	0	0	0	0	0	0	2	5	9	11	15	15	15	15	15	15
64	0	0	0	0	2	5	8	11	15	17	20	23	25	25	25	25	25
128	9	13	17	20	23	26	29	33	36	39	42	45	48	49	49	49	49
256	57	60	65	68	71	74	77	80	83	86	89	92	95	97	97	98	98

Figure 15: Hybrid integrals with $\zeta_A = \zeta_B$ and $\zeta'_A = \zeta'_B$ in double precision

Hybrid integrals: exA'=exA"; exA'=exB+5																	
Accurate decimal places NA=NA'=6 LA=LA'=5 NB=NB'=6 LB = LB' = 5																	
Double precision																	
exA'=exA" exB	0.0025	0.005	0.01	0.03	0.06	0.12	0.25	0.5	1	2	4	8	16	32	64	128	256
0.005	0	1	6	8	11	14	17	21	24	26	29	30	30	30	30	30	30
0.01	0	1	4	7	10	13	16	19	22	25	27	28	29	29	29	29	29
0.03	0	0	1	4	8	10	13	16	20	22	25	25	25	25	25	25	25
0.06	0	0	0	2	5	8	11	15	17	20	23	24	24	24	24	24	24
0.12	0	0	0	0	3	6	9	12	15	19	21	22	22	22	22	22	22
0.25	0	0	0	0	1	4	7	10	13	16	19	20	20	20	20	20	20
0.5	0	0	0	0	0	2	5	8	11	14	17	18	18	18	18	18	18
1	0	0	0	0	0	0	2	6	9	12	15	17	17	17	17	17	17
2	0	0	0	0	0	0	1	4	7	10	13	16	16	16	16	16	16
4	0	0	0	0	0	0	0	1	4	8	10	13	14	14	14	14	14
8	0	0	0	0	0	0	0	0	2	6	9	11	13	13	13	13	13
16	0	0	0	0	0	0	0	0	2	5	8	11	13	13	13	13	13
32	0	0	0	0	0	0	0	2	5	8	11	14	17	17	17	17	17
64	0	0	0	0	1	4	8	12	14	17	20	23	26	27	27	27	27
128	9	12	17	20	23	26	29	32	35	38	42	45	48	51	51	51	51
256	54	57	62	65	68	71	74	77	80	83	86	89	92	95	98	99	100

Figure 16: Hybrid integrals with $\zeta_A = \zeta_B$ and $\zeta'_B = \zeta'_A + 5$ in double precision

Hybrid integrals: exA'=exA"; exB=exA+5																	
Accurate decimal places NA=NA'=6 LA=LA'=5 NB=NB'=6 LB = LB' = 5																	
Double precision																	
exA'=exA" exA	0.0025	0.005	0.01	0.03	0.06	0.12	0.25	0.5	1	2	4	8	16	32	64	128	256
0.005	0	0	5	8	11	14	17	20	23	26	29	30	30	30	30	30	30
0.01	0	0	3	5	9	12	15	18	21	24	27	27	28	27	28	28	28
0.03	0	0	0	3	6	9	12	15	18	21	24	24	24	24	24	24	24
0.06	0	0	0	1	4	7	10	13	16	19	22	23	23	22	22	22	22
0.12	0	0	0	0	2	5	8	11	14	17	20	21	21	21	21	21	21
0.25	0	0	0	0	0	3	6	9	12	15	18	19	19	19	19	19	19
0.5	0	0	0	0	0	1	4	7	10	13	16	17	17	17	17	17	17
1	0	0	0	0	0	0	2	5	8	11	14	15	16	15	16	15	15
2	0	0	0	0	0	0	0	3	6	9	12	14	14	14	14	14	14
4	0	0	0	0	0	0	0	1	4	7	10	12	12	12	12	12	12
8	0	0	0	0	0	0	0	0	3	6	9	11	11	11	11	11	11
16	0	0	0	0	0	0	0	0	3	6	9	11	12	12	12	12	12
32	0	0	0	0	0	0	0	3	6	9	12	15	15	15	15	15	15
64	0	0	0	0	3	6	9	13	16	18	22	25	25	25	25	25	25
128	11	14	19	22	25	28	31	34	37	40	43	46	49	49	49	49	49
256	54	57	62	65	68	71	74	77	80	83	86	89	92	95	96	96	96

Figure 17: Hybrid integrals with $\zeta_B = \zeta_A + 5$ and $\zeta'_A = \zeta'_B + 5$ in double precision

Hybrid integrals: exA=exB; exA'=exB'																	
Accurate decimal places NA=NA'=6 LA=LA'=5 NB=NB'=6 LB = LB' = 5																	
Quadruple precision																	
exA'=exA" exA =exB	0.0025	0.005	0.01	0.03	0.06	0.12	0.25	0.5	1	2	4	8	16	32	64	128	256
0.005	31	35	36	36	36	36	36	36	36	36	36	36	36	36	36	36	36
0.01	28	30	34	35	35	35	35	35	35	35	35	35	35	35	35	35	35
0.03	22	24	30	33	36	36	36	36	36	36	36	36	36	36	36	36	36
0.06	18	21	26	29	32	35	35	35	35	35	35	35	35	35	35	35	35
0.12	16	18	23	26	29	32	36	35	36	35	35	35	36	35	36	35	35
0.25	11	15	19	22	26	29	32	35	35	35	35	35	35	35	35	35	35
0.5	8	12	16	19	22	25	29	32	34	34	35	34	34	34	34	34	34
1	4	7	13	16	19	21	24	28	31	34	34	34	34	34	34	34	34
2	1	4	9	12	15	18	21	24	27	30	34	33	34	33	34	34	34
4	0	2	6	9	12	15	18	21	24	28	30	32	32	32	32	32	32
8	0	0	3	6	9	12	16	18	22	25	27	30	30	30	30	30	30
16	0	0	2	5	8	11	15	17	20	23	27	30	30	30	30	30	30
32	0	0	5	7	11	14	17	20	23	26	30	33	33	34	34	34	34
64	6	8	14	16	19	22	26	29	32	35	38	41	43	43	43	43	43
128	28	31	36	39	42	45	48	51	54	57	60	63	66	67	67	67	67
256	75	78	83	86	89	92	95	98	101	104	107	110	113	115	115	115	115

Figure 18: Hybrid integrals with $\zeta_A = \zeta_B$ and $\zeta'_A = \zeta'_B$ in quadruple precision

Hybrid integrals: exA'=exA"; exA'=exB+5																	
Accurate decimal places NA=NA'=6 LA=LA'=5 NB=NB'=6 LB = LB' = 5																	
Quadruple precision																	
exA'=exA" exB	0.0025	0.005	0.01	0.03	0.06	0.12	0.25	0.5	1	2	4	8	16	32	64	128	256
0.005	16	19	23	27	30	32	37	39	42	45	48	48	48	48	48	48	48
0.01	14	17	22	25	29	31	36	37	40	43	46	46	46	46	46	46	46
0.03	11	14	19	22	25	28	31	35	37	41	43	44	44	44	45	45	45
0.06	9	12	17	20	23	27	29	32	36	38	41	42	42	42	42	42	42
0.12	7	10	15	18	22	25	27	30	33	36	39	41	41	41	40	41	40
0.25	5	8	13	16	19	22	25	28	31	34	37	39	39	39	39	39	39
0.5	3	6	12	15	17	20	23	26	29	32	35	37	37	37	37	37	37
1	1	4	8	11	15	18	21	24	27	30	33	36	36	36	36	36	36
2	0	2	6	9	12	15	19	22	24	27	31	33	34	34	34	34	34
4	0	0	5	7	11	13	17	20	22	26	29	31	32	32	32	32	32
8	0	0	2	5	9	11	15	18	21	24	27	30	32	31	31	32	31
16	0	0	1	5	8	11	14	17	20	23	26	29	32	32	32	32	32
32	0	0	4	7	10	13	16	20	23	26	29	32	34	35	35	35	35
64	5	8	13	17	19	22	26	29	32	35	38	41	44	45	45	45	45
128	28	31	36	39	42	45	48	51	54	57	60	63	66	69	69	69	69
256	72	75	80	83	86	89	92	95	98	101	104	107	110	113	116	117	117

Figure 19: Hybrid integrals with $\zeta_A = \zeta_B$ and $\zeta'_B = \zeta'_A + 5$ in quadruple precision

Hybrid integrals: exA'=exA"; exB=exA+5																	
Accurate decimal places NA=NA'=6 LA=LA'=5 NB=NB'=6 LB = LB' = 5																	
Quadruple precision																	
exA'=exA" exA	0.0025	0.005	0.01	0.03	0.06	0.12	0.25	0.5	1	2	4	8	16	32	64	128	256
0.005	15	19	23	26	29	32	35	38	41	44	47	48	47	48	48	48	48
0.01	13	16	21	24	27	30	33	37	39	42	45	46	46	46	46	46	46
0.03	10	13	18	21	24	27	31	33	36	39	42	43	43	43	43	43	43
0.06	8	11	16	18	22	25	28	31	34	37	40	40	40	40	40	40	40
0.12	6	9	13	17	20	23	26	29	32	35	38	39	39	39	39	39	39
0.25	4	7	12	15	18	21	24	27	30	33	36	37	37	37	37	37	37
0.5	2	5	10	13	15	19	22	25	28	31	34	35	35	35	35	35	35
1	0	3	8	10	14	17	19	23	26	29	32	33	33	34	33	33	33
2	0	1	6	9	12	15	18	21	24	27	30	32	32	32	32	32	32
4	0	0	4	7	10	13	16	19	22	25	28	31	31	31	31	31	31
8	0	0	3	6	9	12	15	18	21	24	27	29	29	29	29	29	29
16	0	0	3	6	9	12	15	18	21	24	27	29	29	29	29	29	29
32	0	1	6	9	12	15	18	21	24	28	30	33	33	33	33	33	33
64	8	10	15	18	21	24	27	32	34	37	39	42	43	43	43	43	43
128	30	33	38	40	44	47	50	53	56	59	62	65	67	67	67	67	67
256	72	75	80	83	86	89	92	95	98	101	104	107	110	113	115	115	115

Figure 20: Hybrid integrals with $\zeta_B = \zeta_A + 5$ and $\zeta'_A = \zeta'_B + 5$ in quadruple precision

9 Exchange integrals

Exchange integrals of STOs are defined as:

$$[\,\chi^{n_A}_{L_A\,M_A}\;\chi^{n_B}_{L_B\,M_B}\,|\,\chi^{n'_A}_{L'_A\,M'_A}\;\chi^{n'_B}_{L'_B\,M'_B}\,] \equiv \int d\mathbf{r} \int d\mathbf{r}'\;\chi^{n_A}_{L_A\,M_A}(\zeta_A,\mathbf{r}_A)\;\chi^{n_B}_{L_B\,M_B}(\zeta_B,\mathbf{r}_B) \times\quad \chi^{n'_A}_{L'_A\,M'_A}(\zeta'_A,\mathbf{r}'_A)\;\chi^{n'_B}_{L'_B\,M'_B}(\zeta'_B,\mathbf{r}'_B)\;\frac{1}{|\mathbf{r}-\mathbf{r}'|} \tag{172}$$

Although the translation method previously exposed can be also used for these integrals, carrying out a double translation, in this case the treatment in terms of ellipsoidal coordinates seems to be better suited, and the algorithm currently implemented is based on this approach. To our knowledge, the first satisfactory solution to these integrals using ellisoidal coordinates was reported by Ruedenberg [29], who proposed a factorization of the integral as a product of two functions, each associated to a charge distribution. The procedure involves a single numerical integration and, unfortunately, fails to give even middle accuracy for high quantum numbers and small exponents. The presence of the numerical integral, though simple, makes it difficult to cover all the combinations of exponents and quantum numbers in a simple way. An alternative was proposed by Maslen and Trefry [30] which leads to some improvement in the performance, but with quite a significant downgrading in the accuracy when increasing quantum numbers.
We propose a better procedure based on ellipsoidal coordinates and the extensive usage of recurrence relations[31] is summarized below.
In this algorithm, the exchange integral are written as:

$$\begin{aligned}[\,\chi^{n_A}_{L_A\,M_A}\;\chi^{n_B}_{L_B\,M_B}\,|\,\chi^{n'_A}_{L'_A\,M'_A}\;\chi^{n'_B}_{L'_B\,M'_B}\,] &= 2\,\pi^2\,(R_{AB}/2)^{n_A+L_A+n_B+L_B+n'_A+L'_A+n'_B+L'_B} \\ &\times \sum_{m=M_+,M_-} (-1)^m\,(1+\delta_{m0}) \sum_{l=|m|}^{\infty} (2l+1)\left[\frac{(l-|m|)!}{(l+|m|)!}\right]^2 \\ &\times \sum_{k=0}^{\substack{n_A+L_A+n_B \\ +L_B-|m|}} \sum_{k'=0}^{\substack{n'_A+L'_A+n'_B \\ +L'_B-|m|}} W_l^{|m|}(k,k';\beta,\beta') \\ &\times J^{n_AL_A|M_A|,n_BL_B|M_B|}_{lkm}(\gamma)\;J^{n'_AL'_A|M'_A|,n'_BL'_B|M'_B|}_{lk'm}(\gamma')\end{aligned} \tag{173}$$

where

$$\begin{aligned} M_+ &= \text{sgn}(M_AM_B)\times(|M_A|+|M_B|) \\ M_- &= \text{sgn}(M_AM_B)\times|\,|M_A|-|M_B|\,| \end{aligned} \tag{174}$$

$$W_l^{|m|}(k,k';\beta,\beta') = \int_1^\infty d\xi\ (\xi^2-1)^{m/2}\ Q_l^m(\xi)\ \left[\xi^k\ e^{-\beta\xi}\ K_{lk'}^m(\beta',\xi) + \xi^{k'}\ e^{-\beta'\xi}\ K_{lk}^m(\beta,\xi)\right] \tag{175}$$

$$K_{lp}^m(x,\xi) = \int_1^\xi d\xi'\ (\xi'^2-1)^{m/2}\ P_l^m(xi')\ \xi'^p\ e^{-x\xi'} \tag{176}$$

$$J_{lkm}^{nLM,n'L'M'}(z) = s_m \sum_{j=0}^{\substack{n+n'+L\\+L'-|m|}} I_{lj}^m(z)\ \Omega_{kjm}^{nL|M|,n'L'|M'|} \tag{177}$$

where s_m and $\Omega_{kmj}^{nL|M|,n'L'|M'|}$ are numerical coefficients whose calculation is summarized in the appendix B, and

$$I_{lp}^m(z) = \int_{-1}^1 d\eta\ (1-\eta^2)^{m/2}\ P_l^m(\eta)\ \eta^p\ e^{-z\eta} \tag{178}$$

Finally:

$$\gamma = (\zeta_A-\zeta_B)\ R_{AB}/2 \quad \beta = (\zeta_A+\zeta_B)\ R_{AB}/2$$
$$\gamma' = (\zeta'_A-\zeta'_B)\ R_{AB}/2 \quad \beta' = (\zeta'_A+\zeta'_B)\ R_{AB}/2$$

It can be seen that both the functions $J_{lkm}^{nLM,n'L'M'}(z)$ and $W_l^{|m|}(k,k';\beta,\beta')$ play an essential role and the efficiency of the the algorithm is determined by their calculation.
According to eq(177), the calculation of the $J_{lkm}^{nLM,n'L'M'}(z)$ requires the $\Omega_{kmj}^{nL|M|,n'L'|M'|}$ coefficients and the $I_{lp}^m(z)$. Since the $\Omega_{kmj}^{nL|M|,n'L'|M'|}$ do not depend on the exponents of the STO, they can be computed once, following the prescription of appendix, and stored. The $I_{lp}^m(z)$ are closely related to the $\phi_l(z)$ functions defined in eq(154), and their efficient computation follows the same scheme as described for those functions.
Nevertheless, it should be noticed that the $J_{lkm}^{nLM,n'L'M'}(z)$ depend on the parameters of the distributions (pairs of STO) whereas the $\Omega_{kmj}^{nL|M|,n'L'|M'|}$ depend on pairs of distributions (four STO). As a consequence, the efficiency of the overall algorithm is determined by the computation of these functions. The algorithm for their efficient calculation is described below.

9.1 Calculation of the functions $W_l^{|m|}(k,k';\beta,\beta')$

The recurrence relation to increase m:

$$
\begin{aligned}
W_l^{m+1}(k,k';\beta,\beta') &= (l-m)\left[\frac{(l+1-m)^2}{2l+1}W_{l+1}^{|m|}(k,k';\beta,\beta')\right. \\
&- \left.(l+m+1)\;W_l^{|m|}(k+1,k'+1;\beta,\beta')\right] \\
&+ \frac{(l+m)^2\;(l+m+1)}{2l+1}\;W_{l-1}^{|m|}(k,k';\beta,\beta') \qquad (179)
\end{aligned}
$$

reduces the problem to evaluating the set of functions with $m = 0$. To compute them, it is better to work with the auxiliary functions:

$$
\begin{aligned}
w_{ll'}^{kk'} &\equiv \int_1^\infty d\xi\; Q_l(\xi)\;\xi^k\;e^{-\beta\xi}\;\int_1^\xi d\xi'\;P_{l'}(\xi')\;\xi'^{k'}\;e^{-\beta'\xi'} \\
&+ \int_1^\infty d\xi\; Q_{l'}(\xi)\;\xi^{k'}\;e^{-\beta'\xi}\;\int_1^\xi d\xi'\;P_l(\xi')\;\xi'^{k}\;e^{-\beta\xi'} \qquad (180)
\end{aligned}
$$

Obviously:

$$
W_l^{|m|}(k,k';\beta,\beta') = w_{ll}^{kk'} \qquad (181)
$$

From the recurrence relation of the Legendre polynomials –see [7] eq 8.733.2– the following recurrence relations for the $w_{ll'}^{kk'}$ can be derived:

$$
(2l'+1)\;w_{ll'}^{k\,k'+1} = (l'+1)\;w_{l\,l'+1}^{kk'} + l'\;w_{l\,l'-1}^{k\,k'} \qquad l' > 0 \qquad (182)
$$

$$
(2l+1)\;w_{ll'}^{k+1\,k'} = (l+1)\;w_{l+1\,l'}^{kk'} + l\;w_{l-1\,l'}^{k\,k'} \qquad l > 0 \qquad (183)
$$

$$
w_{l0}^{k\,k'} = w_{l1}^{k\,k'-1} + \frac{1}{\beta'}\left[K_{l\,k+k'-1}(\beta+\beta') + (k'-1)\;w_{l0}^{k\,k'-1} - w_{l1}^{k\,k'-2}\right] \qquad (184)
$$

$$
w_{l0}^{k\,k'} = w_{l1}^{k-1\,k'} + \frac{1}{\beta}\left[K_{l\,k+k'-1}(\beta+\beta') + (k-1)\;w_{l0}^{k-1\,k'} - w_{l1}^{k-2\,k'}\right] \qquad (185)
$$

with

$$
K_{l\,n}(s) = K_{ln}^0(s,\infty) \qquad (186)
$$

From these equations, it follows that the set of functions $w_{ll}^{kk'}$ can be computed in a numerically stable way from the functions $w_{ll'} \equiv w_{ll}^{00}$. For these functions, the following relations hold:

$$
w_{ll'} = \frac{\beta'}{2l'+1}\left[w_{l\,l'+1} - w_{l\,l'-1}\right] + u_{ll'} \qquad (187)
$$

$$w_{ll'} = \frac{\beta}{2l+1}\left[w_{l+1\,l'} - w_{l-1\,l'}\right] + u_{l'l} \tag{188}$$

where

$$u_{ll'} \equiv u_{ll'}(s) = \int_1^\infty d\xi\; e^{-s\xi}\left[Q_l(\xi)\; P_{l'}^{(-1)}(\xi) - P_l(\xi)\; Q_{l'}^{(-1)}(xi)\right] \tag{189}$$

with

$$P_l^{(-1)}(\xi) = \int_1^\xi d\xi'\; P_l(\xi') = \frac{1}{2l+1}\left[P_{l+1}(\xi) - P_{l-1}(\xi)\right] \tag{190}$$

$$Q_l^{(-1)}(\xi) = \int_1^\xi d\xi'\; Q_l(\xi') = \frac{1}{2l+1}\left[Q_{l+1}(\xi) - Q_{l-1}(\xi)\right] \qquad l > 0 \tag{191}$$

The recursions (187) and (188) are stable neither for ascending nor for descending. Because of it, the bisection algorithm reported in [32] has been used, starting from w_{00}, $w_{0l_{max}}$, $w_{l_{max}0}$ and $w_{l_{max}l_{max}}$. The first three are computed by:

$$\begin{aligned} w_{00}(\beta,\beta') &= \frac{1}{2\,\beta\,\beta'}\Bigg\{e^{\beta-\beta'}\;\Gamma(0,2\beta) + e^{\beta'-\beta}\;\Gamma(0,2\beta') - e^{\beta+\beta'}\;\Gamma[0,2(\beta+\beta')] \\ &+ e^{-(\beta+\beta')}\left[\mathbf{C} + \ln\left(\frac{2\beta\beta'}{\beta+\beta'}\right)\right]\Bigg\} \end{aligned} \tag{192}$$

$\mathbf{C}$ being Euler constant ($0.577\,215\,664$ ...);

$$\begin{aligned} w_{l0}(\beta,\beta') &= \frac{1}{\beta'}\Bigg[e^{-\beta'}\;L_l(\beta) + \nu_{l-1} - e^{\beta+\beta'}\;\sum_{k=0}^{l-1}\frac{(2\beta)^k}{k+1}\;\theta_l^k(\beta)\;\Gamma[-k,2(\beta+\beta')] \\ &- \theta_l^l(\beta)\;\mu_l(\beta',\beta+\beta') \end{aligned} \tag{193}$$

$$w_{0l}(\beta,\beta') = w_{l0}(\beta',\beta) \tag{194}$$

with $l = l_{max}$, and

$$\begin{aligned} L_{l_{max}}(\beta) &= \int_1^\infty d\xi\; e^{-\beta\xi}\; Q_{l_{max}}(\xi) \\ &\simeq \frac{e^{-\beta}}{l_{max}\;(l_{max}+1)}\left[1 - \frac{2\beta}{(l_{max}-1)\;(l_{max}+1)}\right] \end{aligned} \tag{195}$$

$$\theta_l^k(\beta) = \sum_{j=0}^{k}\frac{(l+j)!}{(l-j)!\;j!\;(2\beta)^j} \tag{196}$$

$$\mu_l(x,y) = e^y \sum_{k=l}^{\infty} \frac{(2x)^k}{k+1} \Gamma(-k,2y) \tag{197}$$

$$\Gamma(-n,z) = \int_z^{\infty} dt\ e^{-t}\ t^{-n-1} \tag{198}$$

For $\beta/\beta' < 5$, the following equation is used instead of (197):

$$\begin{aligned} \mu_l(x,y) &= \frac{1}{2x}\left[e^{-y}\ \ln\frac{y}{y-x} + e^{x+y}\ \Gamma(0,2y) - e^{y-2x}\ \Gamma[0,2(y-x)]\right] \\ &- e^y \sum_{k=0}^{l-1} \frac{(2x)^k}{k+1} \Gamma(-k,2y) \end{aligned} \tag{199}$$

The value of l_{max} is fixed as a power of 2 large enough to allow to compute the $w_{l_{max}l_{max}}$ by the first term of its asymptotic series:

$$w_{ll} \simeq \frac{e^{-(\beta+\beta')}}{(\beta+\beta')\ l\ (l+1)} + \cdots \tag{200}$$

9.2 Tests on the accuracy of algorithms for exchange integrals

The above exposed algorithm for exchange integrals have been implemented in FORTRAN at three different levels of accuracy: double precision, quadruple precision and multiprecision[27]. The multiprecision version (with a working precision of 65 decimal digits) has been used as a reference for testing the accuracy of the other two.

Figs 21 to 24 illustrate the accuracy attained in the exchange integrals. As it can be seen, there is a region of intermediate values of the exponents in which some loss of accuracy is found, mainly when the exponents of the functions of a given distribution are different. In fact, it is to be expected that higher the differences between the exponents imply a slower convergence on the series on l of eq(173). Nevertheless, the accuracy loss in the cases tested seems to be not too dramatic and, if higher accuracy is required, the quadruple precision does the job in a very satisfactory way, as it can be appreciated in figs 10 to 12. As a consequence, most integrals can be computed in double precision and the use of quadruple precision can be restricted to those cases in which a significant loss of accuracy has been detected.

Finally, it should be mentioned that algorithms for exchange integrals based on the translation of STO may be an interesting alternative in cases involving charge distributions with a high asymmetry, i.e with one exponent much larger than the other.

Exchange integrals: exA=exB; exA'=exB'															
Accurate decimal places NA=NA'=6 LA=LA'=5 NB=NB'=6 LB = LB' = 5															
Double precision															
exA =exB exA'=exB'	0.005	0.01	0.03	0.06	0.12	0.25	0.5	1	2	4	8	16	32	64	128
0.0025	17	-	-	-	-	-	-	-	-	-	-	-	-	-	-
0.005	17	17	-	-	-	-	-	-	-	-	-	-	-	-	-
0.01	17	17	16	-	-	-	-	-	-	-	-	-	-	-	-
0.03	17	17	16	16	-	-	-	-	-	-	-	-	-	-	-
0.06	17	17	16	16	16	-	-	-	-	-	-	-	-	-	-
0.12	17	17	16	16	16	15	-	-	-	-	-	-	-	-	-
0.25	17	17	16	16	16	15	15	-	-	-	-	-	-	-	-
0.5	17	17	16	16	16	15	15	15	-	-	-	-	-	-	-
1	17	17	16	16	16	16	15	15	15	-	-	-	-	-	-
2	17	17	16	16	16	16	15	15	15	14	-	-	-	-	-
4	17	16	16	16	15	15	15	14	14	14	13	-	-	-	-
8	17	17	16	16	16	15	15	15	14	14	13	11	-	-	-
16	20	20	20	19	19	19	18	18	18	17	16	15	15	-	-
32	31	30	30	29	29	29	29	28	28	28	27	25	25	28	-
64	55	55	54	54	53	53	53	53	52	52	51	49	49	52	63
128	107	107	106	106	105	105	105	105	104	104	103	101	101	104	-

Figure 21: Exchange integrals with $\zeta_A = \zeta_B$ and $\zeta'_A = \zeta'_B$ in double precision

Exchange integrals: exB=exA; exB'=exA'+5															
Accurate decimal places NA=NA'=6 LA=LA'=5 NB=NB'=6 LB = LB' = 5															
Double precision															
exA'=exB' exA	0.0025	0.005	0.01	0.03	0.06	0.12	0.25	0.5	1	2	4	8	16	32	64
0.005	32	31	31	31	30	30	30	29	29	29	29	29	29	33	42
0.01	30	29	29	29	28	28	28	27	27	27	27	27	27	30	41
0.03	27	26	26	26	25	25	25	24	24	24	24	24	24	27	38
0.06	25	24	24	24	23	23	23	23	22	22	22	22	22	26	36
0.12	23	23	22	22	22	21	21	21	20	20	20	20	20	24	34
0.25	21	21	20	20	20	19	19	19	19	18	18	19	19	22	32
0.5	19	19	19	18	18	18	17	17	17	17	17	17	16	20	30
1	18	18	17	17	17	16	16	16	16	15	15	15	15	19	28
2	17	17	16	16	16	16	15	15	15	14	14	13	13	17	27
4	17	16	16	16	15	15	15	14	14	14	14	12	12	15	25
8	17	16	16	16	15	15	14	14	14	14	12	11	11	14	25
16	17	16	16	16	15	15	15	14	14	14	13	12	12	15	25
32	20	20	20	19	19	19	19	18	18	18	17	15	15	19	29
64	31	31	30	30	30	29	29	29	29	29	27	26	26	29	39

Figure 22: Exchange integrals with $\zeta_A = \zeta_B$ and $\zeta'_B = \zeta'_A + 5$ in double precision

Exchange integrals: exB=exA+5; exA'=exB'+5															
Accurate decimal places NA=NA'=6 LA=LA'=5 NB=NB'=6 LB = LB' = 5															
Double precision															
exA exB'	0.005	0.01	0.03	0.06	0.12	0.25	0.5	1	2	4	8	16	32	64	128
0.005	44	42	39	37	35	34	32	31	30	29	29	29	33	44	42
0.01	42	40	37	35	33	32	30	29	28	27	27	27	31	41	41
0.03	39	37	34	32	30	29	27	26	25	24	24	24	28	38	38
0.06	37	35	32	30	28	27	25	24	23	22	22	22	26	37	36
0.12	35	33	30	28	27	25	23	22	21	20	20	20	24	34	34
0.25	34	32	29	27	25	23	21	20	19	19	18	19	22	32	32
0.5	32	30	27	25	23	21	20	19	18	17	16	17	20	31	30
1	31	29	26	24	22	20	19	17	16	15	15	15	19	29	28
2	30	28	25	23	21	19	18	16	15	14	13	13	18	27	27
4	29	27	24	22	20	19	17	15	14	13	11	12	16	26	25
8	29	26	23	21	20	18	16	14	13	12	11	11	15	26	25
16	29	27	24	22	20	18	17	15	13	12	11	12	15	26	25
32	33	31	28	26	24	22	20	19	18	16	15	15	19	30	29
64	43	41	38	36	34	32	31	29	28	27	25	26	29	39	39
128	42	41	38	36	34	32	30	28	27	25	25	25	29	39	-

Figure 23: Exchange integrals with $\zeta_B = \zeta_A + 5$ and $\zeta'_A = \zeta'_B + 5$ in double precision

Exchange integrals: exA=exB; exA'=exB'															
Accurate decimal places NA=NA'=6 LA=LA'=5 NB=NB'=6 LB = LB' = 5															
Quadruple precision															
exA =exB exA'=exB'	0.005	0.01	0.03	0.06	0.12	0.25	0.5	1	2	4	8	16	32	64	128
0.0025	35	-	-	-	-	-	-	-	-	-	-	-	-	-	-
0.005	35	35	-	-	-	-	-	-	-	-	-	-	-	-	-
0.01	35	35	34	-	-	-	-	-	-	-	-	-	-	-	-
0.03	35	35	34	34	-	-	-	-	-	-	-	-	-	-	-
0.06	35	35	34	34	34	-	-	-	-	-	-	-	-	-	-
0.12	35	35	34	34	34	33	-	-	-	-	-	-	-	-	-
0.25	35	35	34	34	34	33	33	-	-	-	-	-	-	-	-
0.5	35	35	34	34	34	33	33	33	-	-	-	-	-	-	-
1	35	35	35	34	34	34	33	33	33	-	-	-	-	-	-
2	35	35	34	34	34	34	33	33	33	33	-	-	-	-	-
4	35	34	34	34	34	33	33	33	32	32	31	-	-	-	-
8	35	34	34	34	33	33	33	33	32	32	31	30	-	-	-
16	38	38	37	37	37	37	36	36	36	36	34	33	33	-	-
32	48	48	48	48	47	47	47	46	46	46	44	43	43	46	-
64	73	73	72	72	71	71	71	70	70	70	69	67	67	70	77
128	125	125	124	123	123	123	123	123	120	116	112	110	109	112	-

Figure 24: Exchange integrals with $\zeta_A = \zeta_B$ and $\zeta'_A = \zeta'_B$ in quadruple precision

Exchange integrals: exB=exA+5; exA'=exB'																	
Accurate decimal places NA=NA'=6 LA=LA'=5 NB=NB'=6 LB = LB' = 5																	
Quadruple precision																	
exA'=exB' exA	0.0025	0.005	0.01	0.03	0.06	0.12	0.25	0.5	1	2	4	8	16	32	64	128	256
0.005	50	50	49	49	49	48	48	48	47	47	47	47	47	50	61	85	132
0.01	48	48	47	47	47	46	46	46	45	45	45	45	45	49	59	83	130
0.03	45	45	44	44	44	43	43	43	42	42	42	42	42	45	56	80	127
0.06	43	43	42	42	42	41	41	41	40	40	40	40	40	44	54	78	124
0.12	41	41	40	40	40	39	39	39	39	38	38	38	38	41	52	76	122
0.25	39	39	39	38	38	38	37	37	37	37	37	36	37	40	50	74	120
0.5	38	37	37	37	36	36	36	35	35	35	35	34	35	38	48	72	117
1	36	36	36	35	35	35	34	34	34	34	33	28	33	25	47	71	115
2	35	35	35	34	34	34	33	33	33	33	32	31	32	35	45	70	113
4	35	34	34	34	34	33	33	33	32	32	31	30	30	33	43	68	111
8	34	34	34	33	33	33	33	32	32	32	30	29	29	33	43	67	110
16	35	35	34	34	34	33	33	33	32	32	31	30	29	33	43	67	110
32	39	39	37	38	37	37	37	37	36	36	35	33	33	36	47	71	113
64	49	49	49	48	47	48	47	47	47	46	45	44	44	47	57	80	-
64	74	73	73	72	72	72	72	71	71	70	70	68	68	71	80	100	-
128	126	125	124	125	124	124	124	123	121	117	113	111	110	113	-	-	-

Figure 25: Exchange integrals with $\zeta_A = \zeta_B$ and $\zeta'_B = \zeta'_A + 5$ in quadruple precision

Exchange integrals: exB=exA+5; exA'=exB'+5																
Accurate decimal places NA=NA'=6 LA=LA'=5 NB=NB'=6 LB = LB' = 5																
Quadruple precision																
exA exB'	0.005	0.01	0.03	0.06	0.12	0.25	0.5	1	2	4	8	16	32	64	128	256
0.005	62	60	57	55	54	52	50	49	48	47	47	47	51	61	86	133
0.01	60	58	55	53	52	50	48	47	46	45	45	45	49	59	84	131
0.03	57	55	52	50	49	47	45	44	43	42	42	42	46	56	81	128
0.06	55	53	50	48	47	45	43	42	41	41	40	40	44	54	79	125
0.12	54	52	48	47	45	43	41	40	39	39	38	38	42	53	77	123
0.25	52	50	47	45	43	41	40	38	38	37	36	36	40	51	75	121
0.5	50	48	45	43	41	40	38	37	36	35	34	35	39	49	73	118
1	49	47	44	42	40	38	37	35	31	34	33	24	37	47	71	116
2	48	46	43	41	39	37	36	31	33	32	31	32	35	46	70	114
4	48	45	42	40	39	37	35	33	32	31	30	30	34	44	69	112
8	47	45	42	39	38	36	34	32	31	30	29	29	25	43	68	111
16	47	45	42	40	38	36	35	25	31	30	29	30	33	44	68	111
32	51	49	46	44	42	40	38	37	35	34	26	33	37	48	72	114
64	61	59	56	54	52	51	49	47	46	44	43	44	47	58	80	-
128	86	84	81	79	77	75	73	72	70	69	68	68	72	80	101	-
256	133	131	128	125	123	121	118	116	114	112	111	111	114	-	-	-

Figure 26: Exchange integrals with $\zeta_B = \zeta_A + 5$ and $\zeta'_A = \zeta'_B + 5$ in quadruple precision

10 Large STO-nG expansions for three- and four-center two-electron integrals

Up to date, the efforts carried out for the direct calculation of three- and four-center two-electron integrals involving STO have not yield sufficiently efficient algorithms yet. Although it is to be expected that these efforts will prove fruitful in the near future and that such efficient algorithms will be designed, the only currently available algorithms for computing these two-electron integrals in the general case are based on the use of large Gaussian expansions of the STO –the so-called STO-nG expansions.

Using these expansions, each integral with STO becomes a linear combination of integrals involving Gaussian type orbitals (GTO), which can be computed by very efficient algorithms.

In order to attain an accuracy in the integrals suitable for molecular calculations, the number of Gaussians per STO can be moderately large (between 10 to 15 in HF calculations, larger for CI calculations) and usual algorithms implemented in standard computational packages cannot be very efficient in this case. In 1996 Prof. K. Ishida developed a new algorithm[33], and has improved it later on. This algorithm has proved to be very efficient when using large STO-nG expansions, and it is currently implemented in SMILES[2].

In the final phase of the current project, new STO-nG expansions have been attained to cover a range of quantum numbers: $0 \leq L \leq 6$ and $L \leq N \leq 9$ except the $0s$) that is sufficient for most cases. Attaining long expansions is not an easy task, mainly for high quantum numbers, and it requires special techniques for minimization of residual funtions depending on a large number of nonlinear (exponential) parameters. In our group we have developed one of such techniques, which is summarized in appendix C.

The expansions obtained in this project have been added to the file with the previously existing ones, and the new file is included in the supplementary material of this report, together with a standalone program for computing two-electron integrals with these expansions.

11 Conclusions

Different algorithms for integrals appearing in molecular integrals with Slater type orbitals (STO) have been coded and their performance has been thoroughly tested regarding their accuracy and computational cost.

In a first step, algorithms for the calculation of two-center one-electron integrals have been formulated, coded and analyzed. The main conclusions of this part were that:

- The algorithms already currently available in SMILES for these integrals, based on recurrence relations, cannot provide sufficient accuracy for large N and L quantum numbers.

- The new algorithm using ellipsoidal coordinates enables to compute these integrals with sufficient accuracy for molecular calculations in a range of values of N and L considerably larger than the previous one.
- An alternative algorithm based on the shift operators technique has been also developed and tested to be used in some algorithms for the computation of Coulomb integrals.

In a second step, the calculation of the two-center coulomb integrals has been dealt with. Since these integrals play a very important role in some formulations of molecular structure calculation, a thorough analysis of the mathematical aspects of the problem was carried out. The formulation in terms of the shift-operators technique, Fourier transform and translation method was carefully revisited and different combinations of these techniques were explored. Finally, three different algorithms were selected for implementation and testing: one based on shift operators, and two different algorithms using the translation of the STO. The main conclusions of this part were:

- The extension to higher quantum numbers of the algorithms already available in SMILES for theseintegrals, based on the translation of STO, implies further parametrization of auxiliary functions, which is a cumbersome process.
- The new algorithm using shift operators leads to serious numerical cancellations for high quantum numbers which cause an important loss of accuracy.
- The new algorithm using translation methods accompanied by a one-dimension numerical integration seems to be more robust and is quite fast, but the dependence of the integrand with both the exponents and quantum numbers of the STO makes it difficult to implement an efficient quadrature scheme for the general case.
- The algorithm using translation methods with analytical integration seems to be the best option in this moment.

In the third step, the hybrid integrals were examined and algorithms based on the translation method were implemented, coded and tested. The main conclusions of this part were:

- The algorithm used in SMILES for hybrid integrals, based on the translation of STO, lead to a serious loss of accuracy for high quantum numbers in the current implementation.
- The new algorithm for hybrid integrals, based also in the translation method but with different procedures for the computation of auxiliary functions, allows to extend the range of applicability to higher quantum numbers, but quadruple precision is mandatory in a broad range of values of the exponents, this being insufficient in some combinations of large and small values of the exponents.

- Algorithms based on the usage of large STO-nG expansions of the STO (see below in this report) can be a provisional alternative for these pathological cases, but a further study of alternative techniques such as those based on ellipsoidal coordinates, seems to be desirable.

The third step was devoted to the computation of exchange integrals with algorithms based on ellipsoidal coordinates. The main conclusion of the analysis were:

- The algorithm used in SMILES for exchange integrals, based on the translation of STO, can be confidently used for moderately high quantum numbers, but changes must be done in the codes.
- The new codes for these integrals allow to extend the range of applicability to higher quantum numbers, the bottleneck being now the size of some intermediate auxiliary matrices, which hinders the usage of multiprecision. Nevertheless, this is not a serious drawback since multiprecision is only used as a testing reference.
- A further effort to redesign the implementation avoiding the use of such large intermediate matrices may be convenient.

Finally, as scheduled in the proposal, new STO-nG expansions were developed to fully cover the range of quantum numbers: $0 \leq L \leq 6$ and $L \leq N \leq 9$ (except the $0s$). These expansions are used for computing three- and four-center molecular integrals with STO and, as commented above, could be useful to cover the pathological cases of hybrid integrals until a better alternative is available.
Instructions for installing and running the programs corresponding to the different algorithms accompanying this report are given in appendix D.

Appendix A. The functions $A_j(\beta)$ and $B_j(\nu)$

The functions $A_j(\beta)$ are closely related to the Euler Incomplete Gamma functions of second type:

$$A_j(\beta) = \int_1^\infty d\xi \; \xi^j \; e^{-\beta\,\xi} = \frac{j!}{\beta^{j+1}} \; e^{-\beta} \; e_j(\beta) \tag{201}$$

where $e_j(\beta)$ is the expansion of the exponential function truncated at j^{th} order.
They can be computed in a fully stable way by ascending recursion:

$$A_j(\beta) = \left[j \; A_{j-1}(\beta) + e^{-\beta} \right] \frac{1}{\beta} \tag{202}$$

The calculation of the $B_j(\nu)$ functions is a bit more difficult. Their main properties are summarized below.
Definition:

$$B_j(\nu) = \int_{-1}^{1} d\eta \; \eta^j \; e^{-\nu\,\eta} \tag{203}$$

Power expansion,
for j even ($j \equiv 2p$):

$$B_{2p}(\nu) = \sum_{i=0}^{\infty} \frac{\nu^{2i}}{(p+1/2+i)\;(2i)!} = \frac{1}{p+1/2}\;{}_1F_2(p+1/2; 1/2, p+3/2; \nu^2/4) \tag{204}$$

for j odd ($j \equiv 2p+1$):

$$B_{2p+1}(\nu) = -\sum_{i=0}^{\infty} \frac{\nu^{2i+1}}{(p+3/2+i)\;(2i+1)!} = \frac{1}{p+3/2}\;{}_1F_2(p+3/2; 3/2, p+5/2; \nu^2/4) \tag{205}$$

Expansion in Bessel functions:
for $j = 2p$ the following identity can be used:

$$(u^2)^p = (u^2 - 1 + 1)^p = \sum_{n=0}^{p} \frac{p!\;(-1)^n}{(p-n)!\;n!}\;(1-u^2)^n \tag{206}$$

and therefore (see [7] eq. 8.431):

$$\begin{aligned} B_{2p}(\nu) &= \sum_{n=0}^{p} \frac{p!\;(-1)^n}{(p-n)!\;n!} \int_{-1}^{1} du\;(1-u^2)^n\;e^{-\nu\,u} \\ &= \sqrt{2\pi}\;\sum_{n=0}^{p} \frac{p!\;(-2)^n}{(p-n)!\;\nu^{n+1/2}}\;I_{n+1/2}(\nu) \end{aligned} \tag{207}$$

For $j = 2p+1$, combining the relation:

$$B_{2p+1}(\nu) = \frac{\partial}{\partial\nu} B_{2p}(\nu) \tag{208}$$

with [7] eq. 8.486.5, it follows:

$$B_{2p+1}(\nu) = -\sqrt{2\pi}\;\nu\;\sum_{n=0}^{p} \frac{p!\;(-2)^n}{(p-n)!\;\nu^{n+3/2}}\;I_{n+3/2}(\nu) \tag{209}$$

Expansion in Gamma functions.
Direct integration of eq(203) yields:

$$B_j(\nu) = 2\,e^{\nu}\,\int_0^1 dt\,(2t-1)^j\,e^{-2\nu t} = (-1)^j\,e^{\nu}\,\sum_{i=0}^{j}\frac{j!\,(-1)^i}{(j-i)!\,i!}\,\frac{\gamma(i+1,2\nu)}{\nu^{i+1}} \tag{210}$$

Recurrence relations.
Integration by parts gives:

$$(j+1)\,B_j(\nu) = e^{-\nu} + (-1)^j\,e^{\nu} + \nu\,B_{j+1}(\nu) \tag{211}$$

This relation, applied twice, gives:

$$(j+1)\,(j+1)\,B_j(\nu) = e^{-\nu}\,(j+2+\nu) + (-1)^j\,e^{\nu}\,(j+2-\nu) + \nu^2\,B_{j+2}(\nu) \tag{212}$$

Iterated application of this process yields:

$$\frac{1}{j!}\,B_j(\nu) = e^{-\nu}\,\sum_{i=0}^{\infty}\frac{(j+2+2i+\nu)}{(j+2+2i)!}\,\nu^{2i} + (-1)^j\,e^{\nu}\,\sum_{i=0}^{\infty}\frac{(j+2+2i-\nu)}{(j+2+2i)!}\,\nu^{2i} \tag{213}$$

or, equivalently:

$$\frac{1}{(2k)!}\,B_{2k}(\nu) = (e^{\nu}+e^{-\nu})\,\sum_{i=0}^{\infty}\frac{1}{(2k+1+2i)!}\,\nu^{2i} - (e^{\nu}-e^{-\nu})\,\sum_{i=0}^{\infty}\frac{1}{(2k+2+2i)!}\,\nu^{2i+1} \tag{214}$$

and

$$\frac{1}{(2k+1)!}\,B_{2k+1}(\nu) = -(e^{\nu}-e^{-\nu})\,\sum_{i=0}^{\infty}\frac{\nu^{2i}}{(2k+2+2i)!} + (e^{\nu}+e^{-\nu})\,\sum_{i=0}^{\infty}\frac{\nu^{2i+1}}{(2k+3+2i)!} \tag{215}$$

The algoritm for $B_j(\nu)$ functions.
The algorithm followed to compute the $B_j(\nu)$ functions consists of the use of upwards recursion from $j = 0$ to $j = E[\nu]$ and downwards recursion from $j = j_{max}$ to $j = E[\nu]$. Upwards recursion starts with:

$$B_0(\nu) = \frac{2\,\sinh(\nu)}{\nu}, \qquad B_0(0) = 2 \tag{216}$$

Downwards recursion starts with $B_{j_{max}}(\nu)$ computed by means of eq(213) with j_{max} taken as the lowest suitable even number to prevent cancellation errors. Convergence of the series is checked and a warning message will be issued if the prescribed convergence (1.d-35 in quadruple precision) is not achieved with the highest allowed number of terms (100). We have never observed that message throughout our tests, i.e. the maximum available number of terms seems to be sufficient for reaching convergence in all cases.

The stability of the recursion scheme was thoroughly tested with Mathematica, working in extended precision, and no loss of accuracy was observed. *The algorithm seems to be fully stable*.

Appendix B. Calculation of the coefficients $\Omega_{kmj}^{nLM,n'L'M'}$

The decomposition of a two-center charge distribution in ellipsoidal coordinates gives:

$$\begin{aligned} r_A\, r_B\, \chi_{LM}^{n}(\mathbf{r}_A,\zeta)\, \chi_{L'M'}^{n'}(\mathbf{r}_B,\zeta') &= \left(\frac{R_{AB}}{2}\right)^{n+n'+L+L'} e^{-\xi\,(\zeta+\zeta')\,R_{AB}/2} \\ \times\quad & e^{-\eta\,(\zeta-\zeta')\,R_{AB}/2}\, \sum_{\mu} s_\mu \Phi_\mu(\phi)\, \left[(\xi^2-1)\,(1-\eta^2)\right]^{|\mu|/2} \\ \times\quad & \sum_{r=0}^{\substack{n+n'+L\\+L'-|\mu|}} \sum_{s=0}^{\substack{n+n'+L\\+L'-|\mu|}} \Omega_{rs\mu}^{nL|M|,n'L'|M'|}\, \xi^r\, \eta^s \end{aligned} \tag{217}$$

where

$$\Phi_\mu(\phi) = \begin{cases} \cos\mu\phi & \mu \geq 0 \\ \sin|\mu|\phi & \mu < 0 \end{cases} \tag{218}$$

$$\sum_{\mu} s_\mu\, \Phi_\mu(\phi) = \Phi_M(\phi)\, \Phi_{M'}(\phi) = s_{M_+}\, \Phi_{M_+}(\phi) + s_{M_-}\, \Phi_{M_-}(\phi) \tag{219}$$

with

$$s_{M_+} = \begin{cases} 1 & \text{if } M=0 \text{ or } M'=0 \\ -1/2 & \text{if sgn}(M)<0 \text{ and } \text{sgn}(M')<0 \\ 1/2 & \text{otherwise} \end{cases} \tag{220}$$

$$s_{M_-} = \begin{cases} 0 & \text{if } M=0 \text{ or } M'=0 \\ 1/2 & \text{if sgn}(M)=\text{sgn}(M') \\ \text{sgn}(M)\ \text{sgn}(|M'|-|M|)\ (1-\delta_{M-M',0})/2 & \text{otherwise} \end{cases} \tag{221}$$

$$M_+ = (|M|+|M'|)\ \text{sgn}(M)\ \text{sgn}(M') \tag{222}$$

$$M_- = \big||M|-|M'|\big|\ \text{sgn}(M)\ \text{sgn}(M') \tag{223}$$

where $\text{sgn}(m)$ stands for the algebraic sign of m times 1.
The $\Omega_{kmj}^{nLM,n'L'M'}$ coefficients can be expressed in terms of $A_{ij}^{nL|M|}$ and $B_{ij}^{nL|M|}$ defined by:

$$r_A^n\ z_L^M(\mathbf{r}_A) = (R_{AB}/2)^{n+L}\ \Phi_M(\phi)\ \left[(\xi^2-1)\ (1-\eta^2)\right]^{|M|/2} \sum_{i=0}^{n+L-|M|}\ \sum_{j=0}^{n'+L'-|M|} A_{ij}^{nL|M|}\ \xi^i\ \eta^j \tag{224}$$

$$r_B^n\ z_L^M(\mathbf{r}_B) = (R_{AB}/2)^{n+L}\ \Phi_M(\phi)\ \left[(\xi^2-1)\ (1-\eta^2)\right]^{|M|/2} \sum_{i=0}^{n+L-|M|}\ \sum_{j=0}^{n'+L'-|M|} B_{ij}^{nL|M|}\ \xi^i\ \eta^j \tag{225}$$

which can be computed by recursion:

$$A_{ij}^{0M|M|} = B_{ij}^{0M|M|} = (2|M|-1)!!\ \delta_{i0}\ \delta_{j0} \tag{226}$$

$$\begin{aligned}(L-|M|+1)\ A_{ij}^{0\,L+1\,|M|} &= (2L+1)\ \left(A_{i-1\,j-1}^{0L|M|} + A_{i\,j}^{0L|M|}\right) \\ -\ \ (L+|M|)\ &\left(A_{i-2\,j}^{0\,L-1\,|M|} + 2\ A_{i-1\,j-1}^{0\,L-1\,|M|} + A_{i\,j-2}^{0\,L-1\,|M|}\right)\end{aligned} \tag{227}$$

$$\begin{aligned}(L-|M|+1)\ B_{ij}^{0\,L+1\,|M|} &= (2L+1)\ \left(B_{i-1\,j-1}^{0L|M|} - B_{i\,j}^{0L|M|}\right) \\ -\ \ (L+|M|)\ &\left(B_{i-2\,j}^{0\,L-1\,|M|} - 2\ B_{i-1\,j-1}^{0\,L-1\,|M|} + B_{i\,j-2}^{0\,L-1\,|M|}\right)\end{aligned} \tag{228}$$

$$A_{ij}^{n+1\,L|M|} = A_{i-1\,j}^{nL|M|} + A_{i\,j-1}^{nL|M|} \tag{229}$$

$$B_{ij}^{n+1\,L|M|} = B_{i-1\,j}^{nL|M|} - B_{i\,j-1}^{nL|M|} \tag{230}$$

The final expression of the $\Omega_{rs\mu}^{nLM,n'L'M'}$ being:

$$\Omega_{rsM_+}^{nLM,n'L'M'} = \sum_{\substack{i=\max(0,r-n\\ -L+|M'|)}}^{\substack{\min(r,\\ n+L-|M|)}}\ \sum_{\substack{j=\max(0,s-n\\ -L+|M'|)}}^{\substack{\min(s,\\ n+L-|M|)}} A_{ij}^{nL|M|}\ B_{r-i\,s-j}^{n'L'|M'|} \tag{231}$$

$$\Omega_{rsM_-}^{nLM,n'L'M'} = \sum_{\substack{i=\max(0,\\ p-r/2)}}^{p}\ \sum_{j=0}^{\min(p,s/2)} \Omega_{r+2i-2p\ s-2j\ M_+}^{nLM,n'L'M'}\ \frac{(-1)^{i+j}\ (p!)^2}{i!\ j!\ (p-i)!\ (p-j)!} \tag{232}$$

with $p = \min(|M|, |M'|)$.

Appendix C. Approximation of functions with basis sets containing a big number of nonlinear parameters

Let us consider the approximation of a function $f(\mathbf{r})$ in terms of a set of functions,$\{\chi_r(\mathbf{r},\boldsymbol{\xi})\}_{r=1}^{m}$, depending on nonlinear parameters, $\boldsymbol{\xi} = (\xi_1, ...\xi_n,)$. For a given $\boldsymbol{\xi}$, the optimal approximation, $f'(\mathbf{r})$, is the projection onto $\boldsymbol{\chi}$:

$$| f'(\mathbf{r}) \rangle = \mathscr{P} \ | f(\mathbf{r}) \rangle \tag{233}$$

with the projector:

$$\mathscr{P} = | \boldsymbol{\chi} \rangle \ \mathbf{S}^{-1} \ \langle \boldsymbol{\chi} | \ = \sum_i \sum_j | \chi_i \rangle \ (\mathbf{S}^{-1})_{ij} \ \langle \chi_j | \tag{234}$$

where $| \boldsymbol{\chi} \rangle = (| \chi_1 \rangle, | \chi_2 \rangle, ... | \chi_m \rangle)$, and the $\mathbf{S}$ is the overlap matrix with elements $S_{rs} = \langle \chi_r | \chi_s \rangle$. The residual will be:

$$\Delta^2 = || \ | f \rangle - \mathscr{P} \ | f \rangle ||^2 = \langle f | 1 - \mathscr{P} | f \rangle \tag{235}$$

and minimizing it with respect to $\boldsymbol{\xi}$:

$$\frac{\partial \Delta^2}{\partial \xi_i} = \frac{\partial}{\partial \xi_i} \langle f | 1 - \mathscr{P} | f \rangle = - \langle f | \frac{\partial \mathscr{P}}{\partial \xi_i} | f \rangle = 0 \qquad i = 1, 2, ...m \tag{236}$$

Furthermore:

$$\frac{\partial \mathscr{P}}{\partial \xi_i} = | \frac{\partial \boldsymbol{\chi}}{\partial \xi_i} \rangle \ \mathbf{S}^{-1} \ \langle \boldsymbol{\chi} | \ + \ | \boldsymbol{\chi} \rangle \ \mathbf{S}^{-1} \ \langle \frac{\partial \boldsymbol{\chi}}{\partial \xi_i} | \ + \ | \boldsymbol{\chi} \rangle \ \frac{\partial \mathbf{S}^{-1}}{\partial \xi_i} \ \langle \boldsymbol{\chi} | \tag{237}$$

where

$$\frac{\partial \mathbf{S}^{-1}}{\partial \xi_i} = -\mathbf{S}^{-1} \ \frac{\partial \mathbf{S}}{\partial \xi_i} \ \mathbf{S}^{-1} = -\mathbf{S}^{-1} \left[\langle \frac{\partial \boldsymbol{\chi}}{\partial \xi_i} | \boldsymbol{\chi} \rangle + \langle \boldsymbol{\chi} | \frac{\partial \boldsymbol{\chi}}{\partial \xi_i} \rangle \right] \mathbf{S}^{-1} \tag{238}$$

Replacing in eq(237) and grouping terms:

$$\frac{\partial \mathscr{P}}{\partial \xi_i} = \ | \boldsymbol{\chi} \rangle \ \mathbf{S}^{-1} \ \langle \frac{\partial \boldsymbol{\chi}}{\partial \xi_i} | \, (1 - \mathscr{P}) + (1 - \mathscr{P}) \, | \frac{\partial \boldsymbol{\chi}}{\partial \xi_i} \rangle \ \mathbf{S}^{-1} \ \langle \boldsymbol{\chi} | \tag{239}$$

and for real functions it turns:

$$g_i = \frac{\partial \Delta^2}{\partial \xi_i} = - \langle f | \frac{\partial \mathscr{P}}{\partial \xi_i} | f \rangle = -2 \langle f | \boldsymbol{\chi} \rangle \ \mathbf{S}^{-1} \ \langle \frac{\partial \boldsymbol{\chi}}{\partial \xi_i} | \, (1 - \mathscr{P}) \, | f \rangle \tag{240}$$

In general, Δ^2 will be a complicated nonlinear function of $\boldsymbol{\xi}$. Eq(240) can be combined with a gradient technique for minimization, but it is preferable to use a second order method. To do this, the second derivatives of the projector can be obtained from eq(237):

$$
\begin{aligned}
\frac{\partial^2 \mathscr{P}}{\partial\xi_j\partial\xi_i} &= |\,\frac{\partial^2\boldsymbol{\chi}}{\partial\xi_j\partial\xi_i}\,\rangle\,\mathbf{S}^{-1}\,\langle\,\boldsymbol{\chi}\,| + |\,\boldsymbol{\chi}\,\rangle\,\mathbf{S}^{-1}\,\langle\,\frac{\partial^2\boldsymbol{\chi}}{\partial\xi_j\partial\xi_i}\,| + |\,\frac{\partial\boldsymbol{\chi}}{\partial\xi_i}\,\rangle\,\mathbf{S}^{-1}\,\langle\,\frac{\partial\boldsymbol{\chi}}{\partial\xi_j}\,| \\
&+ |\,\frac{\partial\boldsymbol{\chi}}{\partial\xi_j}\,\rangle\,\mathbf{S}^{-1}\,\langle\,\frac{\partial\boldsymbol{\chi}}{\partial\xi_i}\,| + |\,\frac{\partial\boldsymbol{\chi}}{\partial\xi_i}\,\rangle\left(\frac{\partial\mathbf{S}^{-1}}{\partial\xi_j}\right)\langle\,\boldsymbol{\chi}\,| + |\,\boldsymbol{\chi}\,\rangle\left(\frac{\partial\mathbf{S}^{-1}}{\partial\xi_i}\right)\langle\,\frac{\partial\boldsymbol{\chi}}{\partial\xi_j}\,| \\
&+ |\,\frac{\partial\boldsymbol{\chi}}{\partial\xi_j}\,\rangle\left(\frac{\partial\mathbf{S}^{-1}}{\partial\xi_i}\right)\langle\,\boldsymbol{\chi}\,| + |\,\boldsymbol{\chi}\,\rangle\left(\frac{\partial\mathbf{S}^{-1}}{\partial\xi_j}\right)\langle\,\frac{\partial\boldsymbol{\chi}}{\partial\xi_i}\,| \\
&+ |\,\boldsymbol{\chi}\,\rangle\left(\frac{\partial^2\mathbf{S}^{-1}}{\partial\xi_j\partial\xi_i}\right)\langle\,\boldsymbol{\chi}\,| \qquad (241)
\end{aligned}
$$

and

$$
D_{ji} = \frac{\partial^2\Delta^2}{\partial\xi_j\partial\xi_i} = \langle\, f\,|\,\frac{\partial^2\mathscr{P}}{\partial\xi_j\partial\xi_i}\,|\, f\,\rangle \qquad (242)
$$

Notice that the first derivatives of $\mathbf{S}^{-1}$ are given by ec(238) and the second, by:

$$
\begin{aligned}
\frac{\partial^2\mathbf{S}^{-1}}{\partial\xi_j\partial\xi_i} &= -\frac{\partial}{\partial\xi_j}\left[\mathbf{S}^{-1}\,\frac{\partial\mathbf{S}}{\partial\xi_i}\,\mathbf{S}^{-1}\right] \\
&= \mathbf{S}^{-1}\left[\frac{\partial\mathbf{S}}{\partial\xi_j}\,\mathbf{S}^{-1}\,\frac{\partial\mathbf{S}}{\partial\xi_i} + \frac{\partial\mathbf{S}}{\partial\xi_i}\,\mathbf{S}^{-1}\,\frac{\partial\mathbf{S}}{\partial\xi_j} - \frac{\partial^2\mathbf{S}}{\partial\xi_j\partial\xi_i}\right]\mathbf{S}^{-1} \qquad (243)
\end{aligned}
$$

where

$$
\frac{\partial^2\mathbf{S}}{\partial\xi_j\partial\xi_i} = \langle\,\frac{\partial^2\boldsymbol{\chi}}{\partial\xi_j\partial\xi_i}\,|\,\boldsymbol{\chi}\,\rangle + \langle\,\boldsymbol{\chi}\,|\,\frac{\partial^2\boldsymbol{\chi}}{\partial\xi_j\partial\xi_i}\,\rangle + \langle\,\frac{\partial\boldsymbol{\chi}}{\partial\xi_j}\,|\,\frac{\partial\boldsymbol{\chi}}{\partial\xi_i}\,\rangle + \langle\,\frac{\partial\boldsymbol{\chi}}{\partial\xi_i}\,|\,\frac{\partial\boldsymbol{\chi}}{\partial\xi_j}\,\rangle \qquad (244)
$$

As an alternative, eq(239) can be used to give:

$$
\begin{aligned}
\frac{\partial^2 \mathscr{P}}{\partial\xi_j\partial\xi_i} &= |\,\frac{\partial\boldsymbol{\chi}}{\partial\xi_j}\,\rangle\,\mathbf{S}^{-1}\,\langle\,\frac{\partial\boldsymbol{\chi}}{\partial\xi_i}\,|\;(1-\mathscr{P}) + (1-\mathscr{P})\;|\,\frac{\partial\boldsymbol{\chi}}{\partial\xi_i}\,\rangle\,\mathbf{S}^{-1}\,\langle\,\frac{\partial\boldsymbol{\chi}}{\partial\xi_j}\,| \\
&+ |\,\boldsymbol{\chi}\,\rangle\;|\,\frac{\partial\mathbf{S}^{-1}}{\partial\xi_j}\,\langle\,\frac{\partial\boldsymbol{\chi}}{\partial\xi_i}\,|\;(1-\mathscr{P}) + (1-\mathscr{P})\;|\,\frac{\partial\boldsymbol{\chi}}{\partial\xi_i}\,\rangle\;|\,\frac{\partial\mathbf{S}^{-1}}{\partial\xi_j}\,\langle\,\boldsymbol{\chi}\,| \\
&+ |\,\boldsymbol{\chi}\,\rangle\;|\;\mathbf{S}^{-1}\,\langle\,\frac{\partial^2\boldsymbol{\chi}}{\partial\xi_j\partial\xi_i}\,|\;(1-\mathscr{P}) + (1-\mathscr{P})\;|\,\frac{\partial^2\boldsymbol{\chi}}{\partial\xi_j\partial\xi_i}\,\rangle\;|\;\mathbf{S}^{-1}\,\langle\,\boldsymbol{\chi}\,| \\
&- |\,\boldsymbol{\chi}\,\rangle\;|\;\mathbf{S}^{-1}\,\langle\,\frac{\partial\boldsymbol{\chi}}{\partial\xi_i}\,|\;\frac{\partial\mathscr{P}}{\partial\xi_j} - \frac{\partial\mathscr{P}}{\partial\xi_j}\;|\,\frac{\partial\boldsymbol{\chi}}{\partial\xi_i}\,\rangle\;|\;\mathbf{S}^{-1}\,\langle\,\boldsymbol{\chi}\,| \qquad (245)
\end{aligned}
$$

If each approximating function depends on a single parameter $\{\chi_s(\mathbf{r},\xi_s)\}_{s=1}^m$:

$$
\frac{\partial\chi_s}{\partial\xi_i} = \delta_{is}\,\frac{\partial\chi_i}{\partial\xi_i} \qquad (246)
$$

Defining:

$$
\mathbf{C}^\dagger = \langle\, f\,|\,\boldsymbol{\chi}\,\rangle = (\langle\, f\,|\,\chi_1\,\rangle, \langle\, f\,|\,\chi_2\,\rangle, \dots) \qquad \mathbf{C} = \langle\,\boldsymbol{\chi}\,|\, f\,\rangle = \begin{pmatrix} \langle\,\chi_1\,|\, f\,\rangle \\ \langle\,\chi_2\,|\, f\,\rangle \\ \vdots \end{pmatrix} \qquad (247)
$$

$$\overline{\mathbf{C}}^{\dagger} = \langle\, f \,|\, \boldsymbol{\chi} \,\rangle\, \mathbf{S}^{-1} \qquad\qquad \overline{\mathbf{C}} = \mathbf{S}^{-1}\, \langle\, \boldsymbol{\chi} \,|\, f \,\rangle \tag{248}$$

$$\mathbf{C}'^{\dagger} = (\langle\, f \,|\, \frac{\partial \chi_1}{\partial \xi_1} \,\rangle, \langle\, f \,|\, \frac{\partial \chi_2}{\partial \xi_2} \,\rangle, \dots) \qquad \mathbf{C}' = \begin{pmatrix} \langle\, \frac{\partial \chi_1}{\partial \xi_1} \,|\, f \,\rangle \\ \langle\, \frac{\partial \chi_2}{\partial \xi_2} \,|\, f \,\rangle \\ \vdots \end{pmatrix} \tag{249}$$

$$\mathbf{C}''^{\dagger} = (\langle\, f \,|\, \frac{\partial^2 \chi_1}{\partial \xi_1^2} \,\rangle, \langle\, f \,|\, \frac{\partial^2 \chi_2}{\partial \xi_2^2} \,\rangle, \dots) \qquad \mathbf{C}'' = \begin{pmatrix} \langle\, \frac{\partial^2 \chi_1}{\partial \xi_1^2} \,|\, f \,\rangle \\ \langle\, \frac{\partial^2 \chi_2}{\partial \xi_2^2} \,|\, f \,\rangle \\ \vdots \end{pmatrix} \tag{250}$$

$$\mathbf{S} = \langle\, \boldsymbol{\chi} \,|\, \boldsymbol{\chi} \,\rangle = \begin{pmatrix} \langle\, \chi_1 \,|\, \chi_1 \,\rangle & \langle\, \chi_1 \,|\, \chi_2 \,\rangle & \dots \\ \langle\, \chi_2 \,|\, \chi_1 \,\rangle & \langle\, \chi_2 \,|\, \chi_2 \,\rangle & \dots \\ \dots & \dots & \dots \end{pmatrix} \tag{251}$$

$$\mathbf{M} = \langle\, \frac{\partial \boldsymbol{\chi}}{\partial \boldsymbol{\xi}} \,|\, \boldsymbol{\chi} \,\rangle = \begin{pmatrix} \langle\, \frac{\partial \chi_1}{\partial \xi_1} \,|\, \chi_1 \,\rangle & \langle\, \frac{\partial \chi_1}{\partial \xi_1} \,|\, \chi_2 \,\rangle & \dots \\ \langle\, \frac{\partial \chi_2}{\partial \xi_2} \,|\, \chi_1 \,\rangle & \langle\, \frac{\partial \chi_2}{\partial \xi_2} \,|\, \chi_2 \,\rangle & \dots \\ \dots & \dots & \dots \end{pmatrix} \tag{252}$$

$$\mathbf{N} = \langle\, \frac{\partial^2 \boldsymbol{\chi}}{\partial \boldsymbol{\xi}^2} \,|\, \boldsymbol{\chi} \,\rangle = \begin{pmatrix} \langle\, \frac{\partial^2 \chi_1}{\partial \xi_1^2} \,|\, \chi_1 \,\rangle & \langle\, \frac{\partial^2 \chi_1}{\partial \xi_1^2} \,|\, \chi_2 \,\rangle & \dots \\ \langle\, \frac{\partial^2 \chi_2}{\partial \xi_2^2} \,|\, \chi_1 \,\rangle & \langle\, \frac{\partial^2 \chi_2}{\partial \xi_2^2} \,|\, \chi_2 \,\rangle & \dots \\ \dots & \dots & \dots \end{pmatrix} \tag{253}$$

$$\mathbf{T} = \langle\, \frac{\partial \boldsymbol{\chi}}{\partial \boldsymbol{\xi}} \,|\, \frac{\partial \boldsymbol{\chi}}{\partial \boldsymbol{\xi}} \,\rangle = \begin{pmatrix} \langle\, \frac{\partial \chi_1}{\partial \xi_1} \,|\, \frac{\partial \chi_1}{\partial \xi_1} \,\rangle & \langle\, \frac{\partial \chi_1}{\partial \xi_1} \,|\, \frac{\partial \chi_2}{\partial \xi_2} \,\rangle & \dots \\ \langle\, \frac{\partial \chi_2}{\partial \xi_2} \,|\, \frac{\partial \chi_1}{\partial \xi_1} \,\rangle & \langle\, \frac{\partial \chi_2}{\partial \xi_2} \,|\, \frac{\partial \chi_2}{\partial \xi_2} \,\rangle & \dots \\ \dots & \dots & \dots \end{pmatrix} \tag{254}$$

the elements of the gradient become:

$$g_i = -2\, \overline{C}_i\, \left[C'_i - \sum_s M_{is}\, \overline{C}_s \right] = -2\, \overline{C}_i\, \left[C'_i - (\mathbf{M}\, \overline{\mathbf{C}})_i \right] \tag{255}$$

(for large expansions $\mathbf{M}\, \overline{\mathbf{C}}$ decays quickly and may lead to accuracy losses). The second order derivatives are:

$$\begin{aligned} D_{ij} \;=\; & -2 \Big\{ \delta_{ij}\, \overline{C}_i\, \left[C''_i - (\mathbf{N}\, \overline{\mathbf{C}})_i \right] + \left[C'_i\, (\mathbf{S}^{-1})_{ij}\, C'_j - \overline{C}_i\, T_{ij}\, \overline{C}_j \right] \\ & - \left[C'_i\, (\mathbf{S}^{-1})_{ij}\, (\mathbf{M}\, \overline{\mathbf{C}})_j + C'_j\, (\mathbf{S}^{-1})_{ji}\, (\mathbf{M}\, \overline{\mathbf{C}})_i \right. \\ & + \left. \overline{C}_j\, (\mathbf{M}\, \mathbf{S}^{-1})_{ji}\, C'_i + \overline{C}_i\, (\mathbf{M}\, \mathbf{S}^{-1})_{ij}\, C'_j \right] \\ & + \left[\overline{C}_i\, (\mathbf{M}\, \mathbf{S}^{-1}\, \mathbf{M}^{\dagger})_{ij}\, \overline{C}_j + (\mathbf{M}\, \overline{\mathbf{C}})_i\, (\mathbf{S}^{-1})_{ij}\, (\mathbf{M}\, \overline{\mathbf{C}})_j \right. \\ & + \left. \overline{\mathbf{C}}_j\, (\mathbf{M}\, \mathbf{S}^{-1})_{ji}\, (\mathbf{M}\, \overline{\mathbf{C}})_i + \overline{\mathbf{C}}_i\, (\mathbf{M}\, \mathbf{S}^{-1})_{ij}\, (\mathbf{M}\, \overline{\mathbf{C}})_j \right] \Big\} \end{aligned} \tag{256}$$

Appendix D. Installing and running the codes

The `*_global_*.f90` file containing the modules always must be compiled first with a suitable FORTRAN compiler. In case of the quadruple precision code, the compiler must admit this possibility.
Once the corresponding object and the `.mod` files have been generated, the file containing the code of the algorithm must be compiled, and the resulting objects must be linked.
In case of the *multiprecision* version, the Fortran-90 Multiprecision System (`mpfun90`) must be installed in the computer. This package, created and maintained by David H. Bailey, is freely distributed and, in the moment this report is being made, it can be downloaded in the URL: `http://crd.lbl.gov/ dhbailey/mpdist/` Instructions for installation and usage of the *multiprecision* system can be found within the package.
The link instruction for multiprecision must include the path to the directory where the modules specific of `mpfun90` reside. Beware that these modules have been created with the same compiler to be used for compiling the sources for hybrid or exchange integrals.
To run the programs, just proceed as usual: write the executable name followed by the inputfile and the output file preceded by $<$ and $>$ respectively.
We are also including input samples and their corresponding output files for testing that installation has been succesful, and as a guide.
Hereafter, some simple examples of installation and run follow. In all of them, we will assume that Intel's `ifort` FORTRAN90 compiler will be used. For other compilers, make the suitable changes (notice the comments above for the quadruple precision version).
Example 1: installing and running `hybrid_2010_D`
Type the following:

```
ifort -O3 -c hybrid_2010_global_D.f90
ifort -O3 hybrid_2010_D.f90 hybrid_2010_global_D.o -o hybrid_2010_D
hybrid_2010_D < hybrid_2010_D.inp > outputfile_D
```

Compare the content of `outputfile_D` with that of `hybrid_2010_D.out` coming with this report.
Example 2: installing and running `hybrid_2010_mp` (*multiprecision*)
In this example, we will suppose that `mpfun90` has been installed in the system and that its corresponding modules and objects reside in a directory named `/lib/mpfun/f90/`. Type the following:

```
ifort -O3 -c -I/lib/mpfun90/f90 hybrid_2010_global_mp.f90
ifort -O3 -I/lib/mpfun90/f90 /lib/mpfun90/f90/mp*.o hybrid_2010_global_mp.o
```

```
hybrid_2010_mp.f90 -o hybrid_2010_mp

hybrid_2010_mp < hybrid_2010_mp.inp > outputfile_mp
```

Compare the content of `outputfile_mp` with that of `hybrid_2010_mp.out`. Further assistance can be found in `rafael.lopez@uam.es`.

Supplementary material

A tar file compressed with gzip (*EOARD_093069_b.tgz*), accompanying this report, contains the files mentioned in it.
Extract the content, with
`tar -vxzf EOARD_093069_b.tgz`
or alternatively with
`gunzip EOARD_093069_b.tgz`
followed by
`tar -vxf EOARD_093069_b.tar`
it will create a directory named *EOARD_093069* with the following files:
oneelectrelips-Q.f90
oneelectrelips-Q.inp
oneelectrelips-Q.out
coulomb_2010_shiftop_D.f90
coulomb_2010_shiftop_global_D.f90
coulomb_2010_shiftop_D.inp
coulomb_2010_shiftop_D.out
coulomb_2010_intnum_D.f90
coulomb_2010_intnum_global_D.f90
coulomb_2010_intnum_D.inp
coulomb_2010_intnum_D.out
coulomb_2010_transl_D.f90
coulomb_2010_transl_global_D.f90
coulomb_2010_transl_D.inp
coulomb_2010_transl_D.out
coulomb_2010_transl_Q.f90
coulomb_2010_transl_global_Q.f90
coulomb_2010_transl_Q.inp
coulomb_2010_transl_Q.out
coulomb_2010_transl_mp.f90
coulomb_2010_transl_global_mp.f90
hybrid_2010_D.f90
hybrid_2010_global_D.f90
hybrid_2010_D.inp
hybrid_2010_D.out
hybrid_2010_Q.f90
hybrid_2010_global_Q.f90

hybrid_2010_Q.inp
hybrid_2010_Q.out
hybrid_2010_mp.f90
hybrid_2010_global_mp.f90
hybrid_2010_mp.inp
hybrid_2010_mp.out
exchange_2010_D.f90
exchange_2010_global_D.f90
exchange_2010_D.inp
exchange_2010_D.out
exchange_2010_Q.f90
exchange_2010_global_Q.f90
exchange_2010_Q.inp
exchange_2010_Q.out
exchange_2010_mp.f90
exchange_2010_global_mp.f90
exchange_2010_mp.inp
exchange_2010_mp.out
stngexp_2010.f
stogto_2010.f90
stogto_2010.inp
stogto_2010.out

References

[1] J. F. Rico, R. López, I. Ema, and G. Ramírez, J Comput Chem 25, 1987 (2004).

[2] J. F. Rico, I. Ema, R. López, G. Ramírez, and K. Ishida, SMILES: A package for molecular calculations with STO software, third generation (Transworld Research Network, Kerala (India)), Recent Advances in Computational Chemistry: Molecular Integrals over Slater Orbitals.

[3] Material Modeling for Rocket Propulsion, AFRL/RZSP, ADA♯ 435038 DTIC, Washington, DC

[4] Potential Energy Surfaces, ACS Symposium ♯828, Washington DC (2002)

[5] G. J. Vázquez, J. M. Amero, H. P. Liebermann, R. J. Buenker, and H. Lefebvre-Brion J. Chem. Phys. 126, 164302 (2007)

[6] J. M. Spotts, C.-K. Wong, M. S. Johnson, and M. Okumura, J. A. Boatz, R. J. Hinde, J. A. Sheehy, and P. W. Langhoff J. Phys. Chem. A 107, 6948 (2003)

[7] I. S. Gradshteyn and I. M. Ryzhik, Table of Integrals, Series and Products (Academic Press, New York, 1980), 4th ed.

[8] Fernández Rico, J.; Fernández, J. J.; López, R.; Ramírez, G. Int. J. Quantum Chem. 2000, 78, 137-145.

[9] Fernández Rico, J.; Fernández, J. J.; López, R.; Ramírez, G. Int. J. Quantum Chem. 2000, 78, 83-93.

[10] Fernández Rico, J.; López, R.; Ramírez, G. J. Mol. Struct. Theochem. 2001, 537, 27-40.

[11] Hobson, E. W. The Theory of Spherical and Ellipsoidal Harmonics, Ed. Chelsea, New York, 1965.

[12] Barnett, M.P.; Coulson, C.A. Phil. Trans. Roy. Soc., London A. 243, 221-249, (1951).

[13] Barnett, M. P.; in *Methods of Computational Physics vol 2*, 95, Adler, B; Fernbach, S.; Rotenberg, M., Eds, Academic Press, New York, 1963.

[14] Shull, H.; Löwdin, P. O. J. Chem. Phys. 23, 1392, (1955)

[15] Löwdin, P. O.; Shull, H. Phys. Rev. 101, 1730, (1956)

[16] Watson, G. N. *A Treatise on the theory of Bessel Functions*, 2nd ed., Cambridge University Press, Cambridge, UK, 1966.

[17] Weniger, E. J.; Steinborn, E. O. J. Math. Phys. 30, 774-784 (1989).

[18] Fernández, J.J.; López, R.; Ema, I.; Ramírez, G.; Fernández Rico, J. Int. J. Quantum Chem. 106, 1986-1997, (2006).

[19] Ema, I.; López, R.; Fernández, J.J.; Ramírez, G.; Rico, J.F. Int J Quantum Chem 108, 25-39, (2008)

[20] Fernández Rico, J.; López, R.; Ema, I.; Ramírez, G. J. Comput. Chem. 2005, 26, 846-855.

[21] Fernández Rico, J.; López, R. J. Chem. Phys. 1986, 85, 5890-5894.

[22] Fernández Rico, J.; López, R.; Ramírez, G. Int. J. Quantum Chem. 1988, 34, 121-131.

[23] Homeier, H.H.H. ; Weniger, E.J.; Steinborn, E.O. Int. J. Quantum Chem. 1992, 44, 405-411.

[24] Guseinov, I.I; Mamedov, B.A. Int. J. Quantum Chem. 2000, 78, 146-152.

[25] Guseinov, I. J. Mol. Model. 2003, 9, 135-141; 190-194.

[26] Fernández Rico, J. ; López, R.; Ema, I.; Ramírez, G.; Studies in Physica and Theoretical Chemistry, vol 77 (A), S. Fraga ed., pp 241-272, elsevier 1992.

[27] D.H. Bailey, RNR Technical Report, RNR 94-013, january 1995.

[28] Wimp, J. *Computation with Recurrence Relations*, Pitman, Boston, 1984.

[29] Ruedenberg, K. J. Chem. Phys. 1951, 19, 1459-1477.

[30] Maslen, E.N.; Trefry, M.G. Int. J. Quantum Chem. 1990, 37, 51-68.

[31] Fernández Rico, J.; López, R.; Ramírez, G.; Tablero, C. J Chem Phys 1994, 101, 9807-9816.

[32] Fernández Rico, J.; López, R.; Ramírez, G. Theoret. Chim. Acta 1993, 85, 101-107

[33] Ishida, K. Int. J. Quantum Chem. 1996, 59, 209-218.

[34] Ishida, K. J. Chem. Phys. 1998, 109, 881-890.

[35] Ishida, K. Int. J. Quantum Chem. 2000, 76, 396-406.

[36] Ishida, K. J. Chem. Phys. 2000, 113, 7818-7829.

[37] Ishida, K. J. Comput. Chem. 2002, 23, 378-393.